Ancillary ligand effects in organoyttrium chemistry

Duchateau, Robbert

5 Synthesis and Reactivity of Bis(Alkoxysilylamido) Yttrium η^2-Pyridyl and η^2-α-Picolyl Compounds.*

5-1. Introduction.

In the previous chapter, some aspects of the stability and reactivity of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ (4.6) have been discussed. It was found that the alkoxysilylamido ligands are not inert but instead are quite reactive. For instance, the presence of active hydrogens on substrate molecules (e.g. HC≡CR) leads to protonation and loss of the alkoxysilylamine, $Me_2Si(N(H)CMe_3)(OCMe_3)$. Other less attractive features are the facile exchange of alkoxysilylamido ligands between metal centres (leading to disproportionation) and the limited thermal stability (leading to degradation of the alkoxysilylamido ligands). These examples clearly demonstrate that the bis(alkoxysilylamido) yttrium ligand environment is much more labile than the others described in this thesis.

If a study of the properties of the Y-C bond in $[Me_2Si(NCMe_3)(OCMe_3)]_2YR$ complexes is to be successful, a number of criteria should be satisfied:

(i) The reactivity of the Y-C bond should be favored with respect to the metal ligand bonds. Hence, the Y-C bond should be more reactive than in $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$-$CH(SiMe_3)_2$ (4.6).

(ii) No substrates with acidic protons should be used and to avoid complications due to thermal degradation of the alkoxysilylamido ligand system, temperatures should be kept below 60 - 70^{o}C.

(iii) The tendency to disproportionate should be minimized. Therefore, reactions should be carried out in non-polar solvents and Lewis acidic substrates, such as $LiAlH_4$ (Chapter 2) should be avoided.

* This work has been performed in collaboration with E. A. C. Brussee. The X-ray structure determinations described in this chapter were carried out by A. Meetsma (University of Groningen).

The first part of this chapter deals with the synthesis and characterization of bis(N,O-bis(tert-butyl)alkoxydimethylsilylamido) yttrium pyridyl and (substituted) α-picolyl complexes. The chelating bonding of these carbyls does not only stabilize the complexes, but the presence of ring strain is expected toincrease the reactivity of the Y-C bond. Later, the X-ray crystal structure of the picolyl derivative, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$, will be described in detail. In the second part, the reactivity of these complexes towards dihydrogen and unsaturated substrates will be discussed.

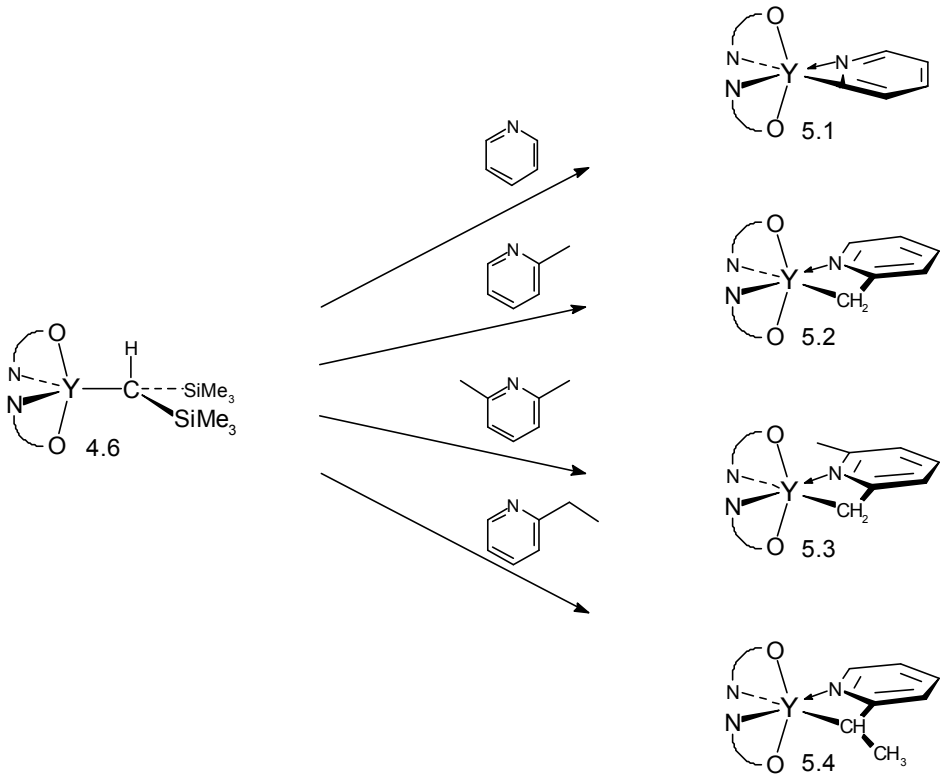
5-2. Synthesis and Characterization of Sterically Unhindered Bis(Alkoxysilylamido) Yttrium Carbyl Species.

Activation of C-H Bonds in Activated Arenes. Aromatic substrates (benzene, toluene, mesitylene; C_6H_5X (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, $P(=CH_2)Ph_2$); pyridine, α-picoline) quite readily undergo (ortho-) metalation by coordinatively unsaturated early transition metal and lanthanide complexes such as Cp^*_2LnR,[1,2] Cp_2TiR[3] and $[Cp_2ZrR.(L)]^+$ [4] (R = H, alkyl, L = Lewis base). This metalation forms a very clean route to alkyl/aryl derivatives, and from a synthetic point of view, is to be preferred over salt metathesis which for the systems under study normally results in mixtures containing salt and solvent molecules.[5] Since the metalation method offers an attractive possibility to generate alkyl/aryl complexes, with M-C bonds more reactive than in the bis(trimethylsilyl)methyl derivative 4.6, it was decided to study the reactivity of 4.6 towards (functionalized) arenes.

As observed for the bis(N,N'-bis(trimethylsilyl)benzamidinato) yttrium complexes, $[C_6H_5C(NSiMe_3)_2]_2YR$ (R = $CH_2Ph.THF$ (2.7), $CH(SiMe_3)_2$ (2.8), μ-H (2.9), Chapter 2, 3), heating of 4.6 in aliphatic or aromatic solvents did not lead to metalation (nor H/D scrambling).[1e] Intramolecular σ-bond metathesis, as part of the thermolysis of 4.6, takes place instead (Chapter 4). In an attempt to make intermolecular C-H bond activation more favorable, complex 4.6 was treated with activated arenes. While with functionalized arenes, C_6H_5X (X = OMe, CH_2NMe_2),[1e] no reaction was observed, treatment of 4.6 with (ortho-substituted) pyridines (NC_5H_5, 2-Me-NC_5H_4, 2,6-Me_2-NC_5H_3, 2-Et-NC_5H_4)[1-4] did indeed lead to the corresponding metalation products (5.1 - 5.4, Scheme 1). However, yields were low to moderate (5.1: 9 %; 5.2: 72 %; 5.3: 65 %, 5.4: 65 %), due to thermolysis of 4.6 and the metalation products 5.1 - 5.4. Interestingly, reaction of 4.6 with α-picoline and 2-ethyl-pyridine

yielded exclusively the α-metalated products 5.2 and 5.4, respectively. This is similar to the reaction of $[C_6H_5C(NSiMe_3)_2]_2YR$ (R = $CH_2Ph.THF$ (2.7), $CH(SiMe_3)_2$ (2.8), μ-H (2.9)) with α-picoline (Chapter 3), but in marked contrast with $Cp^*_2YMe.THF$[1c] or $[Cp_2ZrMe.THF]^+$,[4] which selectively afford the pyridyl compounds $Cp^*_2Y(\eta^2$-(C,N)-2-NC_5H_3-6-Me) and $[Cp_2Zr(\eta^2$-(C,N)-2-NC_5H_3-6-Me).$(THF)]^+$, respectively.

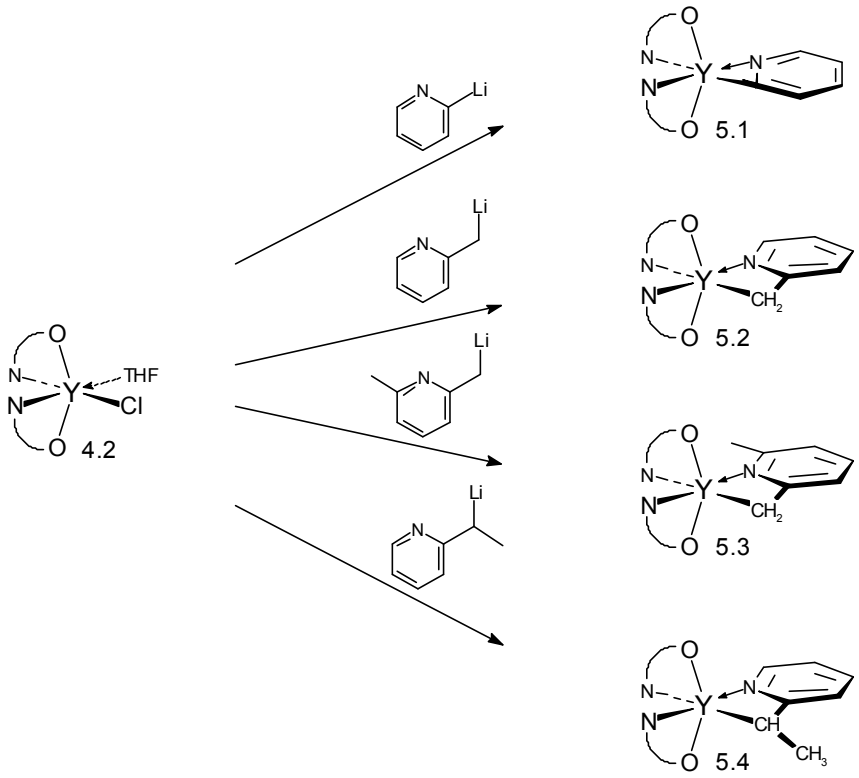
Scheme 1.



Chloride Metathesis of 4.2 with Alkylation Reagents. Intrigued by the chemistry of $Cp^*_2Ln(\eta^2$-(C,N)-2-NC_5H_4) (Ln = Sc, Y, Lu),[1,2] $[Cp_2Zr(\eta^2$-(C,N)-2-$NC_5H_4)]^+$ [4,6] and $Cp_2Zr(\eta^2$-(C,N)-CH_2-2-NC_5H_3-6-Me)]$^+$,[4,7] other strategies to synthesize the metalation products 5.1 - 5.4 were studied. Since all previous attempts to synthesize sterically unhindered bis(alkoxysilylamido) yttrium alkyls by chloride metathesis failed (Chapter 4), the successful reaction of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCl.THF$ 4.2 with pyridyl- and (substituted) α-picolyl lithium[8] was rather surprising (Scheme 2). The compounds $[Me_2Si(NCMe_3)(OCMe_3)]_2YR$ (R = η^2-(C,N)-2-NC_5H_4 (5.1), η^2-(C,N)-CH_2-2-NC_5H_4 (5.2), η^2-(C,N)-CH_2-2-NC_5H_3-6-Me (5.3),

η^2-(C,N)-C(H)Me-2-NC_5H_4 (5.4)) could be isolated in moderate to high yields as red-brown or yellow crystals. It is likely that the bidentate bonding of the pyridyl and picolyl ligands (vide infra) prevents complexation of salt and solvent molecules.

Scheme 2.



Characterization of 5.1 - 5.4. All compounds are very air sensitive and are extremely soluble in common organic solvents (pentane, toluene, THF). They are stable at room temperature but thermolyze at higher temperatures (T > 60°C), analogous to 4.6, to give isobutene, $Me_2Si(N(H)CMe_3)(OCMe_3)$, the corresponding (substituted) pyridine and unknown organometallic products. Spectroscopic and analytical data of compounds 5.1 - 5.4 are collected in the Experimental Section and only the most interesting features will be discussed here. The NMR data correspond well with those of $Cp^*_2Ln(\eta^2$-(C,N)-2-$NC_5H_4)$ (Ln = Sc,[1b,d] Y,[1c,2] Lu[1a]), $[Cp_2Zr(\eta^2$-(C,N)-2-NC_5H_4-6-R)]$^+$ (R = H, Me)[4] and $[Cp_2Zr(\eta^2$-(C,N)-CH_2-2-NC_5H_3-6-Me)]$^+$,[4] respectively. Furthermore, the ^{1}H and ^{13}C NMR spectra of the pyridyl fragment of 5.2 are nearly identical to those of $[C_6H_5C(NSiMe_3)_2]_2Y(\eta^2$-(C,N)-$CH_2$-2-$NC_5H_4)$ (3.18, Chapter 3). Due to the yttrium coupling, the resonance of the ipso-carbon of the pyridyl group in 5.1 appears as a doublet (δ = 226.0 ppm, $^1J_{Y\text{-}C}$ = 26 Hz). For the picolyl complex

(5.2), the α-CH_2 group emerges as a doublet (δ = 2.73 ppm, $^2J_{Y-H}$ = 0.9 Hz) in the ^{1}H NMR spectrum and as a double-triplet (δ = 52.3 ppm, $^1J_{C-H}$ = 143 Hz, $^1J_{Y-C}$ = 6 Hz) in the ^{13}C NMR. The observed $^1J_{Y-C}$ in 5.2 is very small compared with other yttrium carbyl species (bridging carbyls: $^1J_{Y-C}$ = 18 - 21 Hz; terminal carbyls: $^1J_{Y-C}$ = 23 - 74 Hz; Chapter 2) and suggests a weak interaction between the methylene fragment and yttrium (vide infra). Since the NMR spectra of 5.1 - 5.4 are in close analogy with those of the corresponding $Cp^*_2Ln(\eta^2$-(C,N)-$NC_5H_4)$ (Ln = Sc, Y, Lu),[1a,d] $[Cp_2Zr(\eta^2$-(C,N)-2-NC_5H_3-6-Me).$(PMe_3)]^+$[6c] and $[Cp_2Zr(\eta^2$-(C,N)-C(H)Me-2-NC_5H_3-6-Et)$]^+$[7b] systems, we assume that the pyridyl and picolyl fragments are also η^2-bonded in the complexes 5.1 - 5.4. The spectroscopic data of 5.3 and 5.4 show no remarkable features and with chemical shifts and $^1J_{Y-C}$ values comparable to 5.2, they are assumed to be structurally very similar to 5.2.

Tabel I. Selected bond distances and angles for $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-$CH_2$-2-$NC_5H_4)$ (5.2).

Distances (Å)		Angles (deg.)	
Y(1)-O(1)	2.427(4)	Si(1)-Y(1)-Si(2)	138.46(4)
Y(1)-O(2)	2.498(4)	O(1)-Y(1)-N(2)	64.83(12)
Y(1)-N(2)	2.269(4)	O(2)-Y(1)-N(3)	63.53(12)
Y(1)-N(3)	2.243(3)	O(1)-Y(1)-O(2)	174.21(11)
Y(1)-N(1)	2.389(3)	N(2)-Y(1)-N(3)	108.63(13)
Y(1)-C(6)	2.632(5)	O(1)-Y(1)-C(5)	89.62(12)
N(1)-C(1)	1.349(6)	O(2)-Y(1)-C(5)	95.77(12)
N(1)-C(5)	1.386(6)	Y(1)-C(6)-C(5)	84.4(3)
C(1)-C(2)	1.361(7)	N(2)-Y(1)-C(5)	122.59(13)
C(2)-C(3)	1.402(8)	N(3)-Y(1)-C(5)	128.79(13)
C(3)-C(4)	1.359(7)	N(1)-Y(1)-C(6)	56.30(14)
C(4)-C(5)	1.406(7)	N(1)-C(5)-C(6)	115.9(4)
C(5)-C(6)	1.420(7)		

Molecular Structure of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-$CH_2$-2-$NC_5H_4$ (5.2). To elucidate the bonding mode of the α-picolyl fragment, an X-ray structure determination of 5.2 was carried out.[9] A PLUTO drawing of the molecular structure of 5.2 is shown in Figure 1 and

selected bond distances and angles are listed in Table I. At first sight, the coordination geometry around yttrium appears to be octahedral. However, the observed angles show a large deviation from the expected 90°. Therefore, it is more satisfactory to consider the α-picolyl fragment to occupy one coordination vertex, so that the yttrium environment can be regarded as distorted trigonal-pyramidal, with the alkoxysilylamido nitrogens (N(2), N(3)) and the picolyl carbon C(5) forming a tilted equatorial plane (N(2)-Y(1)-N(3) = 108.63(13)°, N(2)-Y(1)-C(5) = 122.59(13)°, N(3)-Y(1)-C(5) = 128.79(13)°, O(1)-Y(1)-O(2) = 174.21(11)°, O(1)-Y(1)-C(5) = 89.62(12)°, O(2)-Y(1)-C(5) = 95.77(12)°).

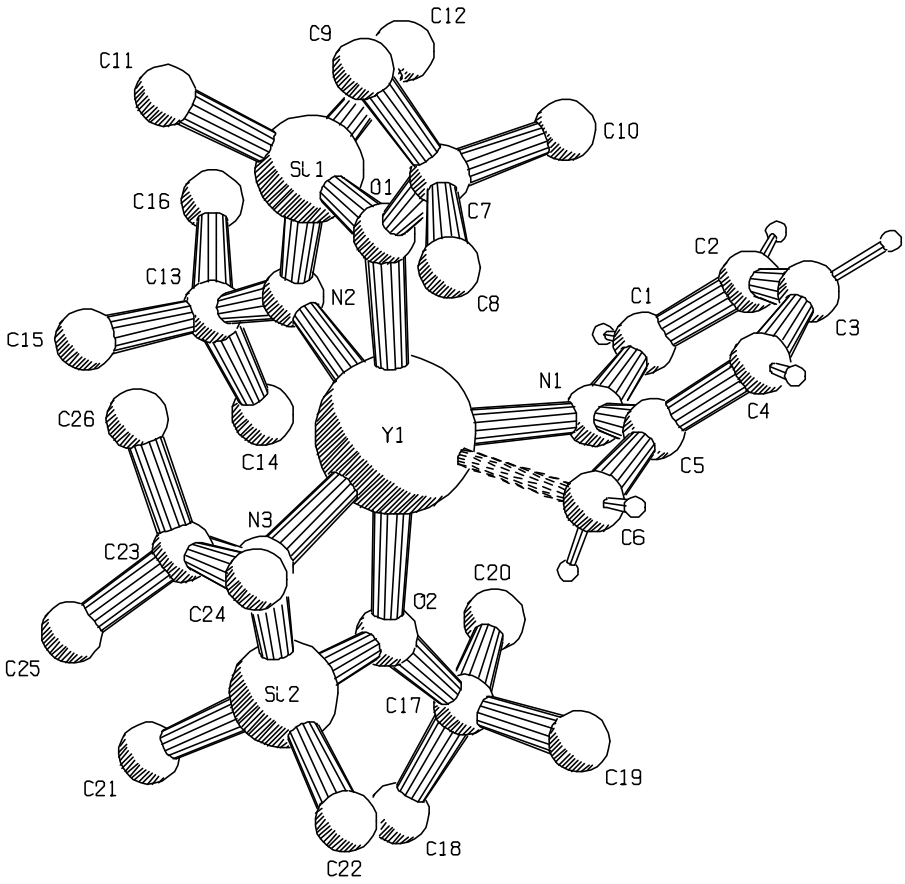


Figure 1. PLUTO drawing of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$ (5.2). Only selected hydrogens are shown for clarity.

The bonding of the ancillary ligands in 5.2 is similar to that found in other crystallographically characterized bis(N,O-bis(tert-butyl)alkoxysilylamido) yttrium (Chapter 4) and lanthanide[10] derivatives. The alkoxysilylamido ligands form almost planar rings with the yttrium atom

(torsion angle: N(2)-Y(1)-O(1)-Si(1) = -2.98(13)^o, N(3)-Y(1)-O(2)-Si(2) = -3.44(14)^o). The Y(1)-N(2) (2.269(4) Å) and Y(1)-N(3) (2.243(3) Å) distances are comparable to the Y-N σ-bond in $Cp^*_2YN(SiMe_3)_2$ (2,274(5) Å, 2.253(5) Å)[11] and indicate substantial π-interaction of the nitrogen lone-pairs with the electrophilic yttrium. In contrast, the Y(1)-O(1) (2.427(4) Å) and Y(1)-O(2) (2.498(4) Å) bonds are rather long.[12] The short Y-N and long Y-O bonds in 5.2 are in good agreement with the calculated Y-N and Y-O bonding character in the model $[H_2Si(NH)(OH)]_2YCH_3$ (Chapter 7) and indicate that the ligands are mainly bonded through the Y-N bonds.

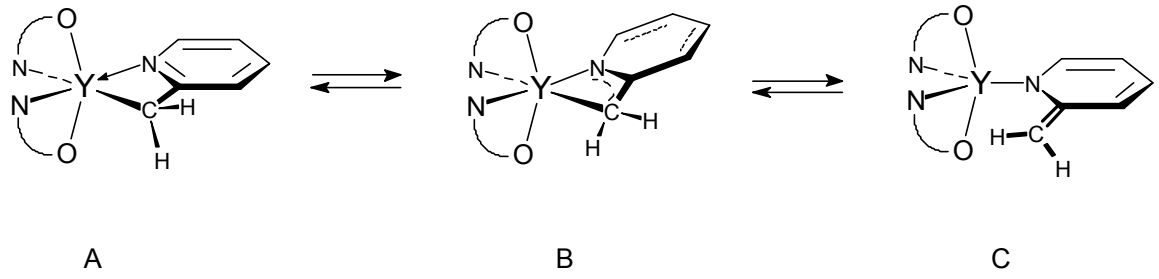


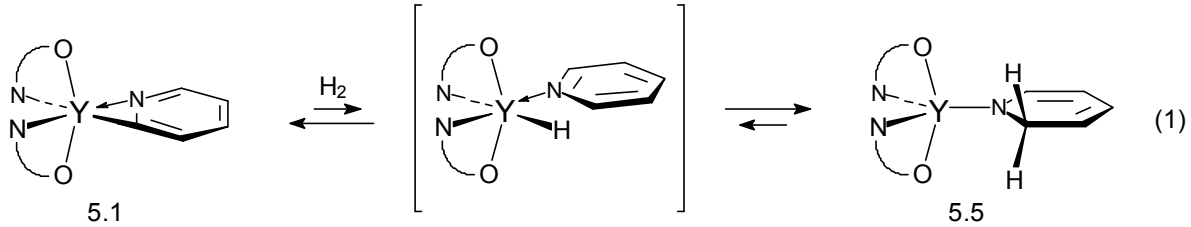
Figure 2.Different bonding modes of the α-picolyl fragment: η^2-alkyl-amine (A), η^3-(C,C,N)-aza-allyl (B), η^1-amido-olefin (C).

Of particular interest is the bonding of the (planar) α-picolyl fragment to yttrium. The Y(1)-C(6) bond (2.632(5) Å) is notably longer than other reported non-bridging Y-C bonds (ranging from 2.38(2) Å[13] - 2.558(19) Å, see Chapter 4), whereas the Y(1)-N(1) bond (2.389(3) Å) is very short for an Y←:N(sp^2) donative bond.[14] The weak Y(1)-C(6) interaction is supported by the small coupling constant ($^1J_{Y\text{-}C}$ = 6 Hz) when compared with other yttrium carbyl species (vide supra). The four-membered (Y(1)-N(1)-C(5)-C(6)) ring is folded over an angle of 139.5^o along the N(1)-C(6) vector. As a result, the yttrium atom is located 1.55 Å out of the pyridine plane. Hence, the bonding of the α-picolyl fragment is best described as an distorted η^3-(C,C,N)-aza-allylic interaction. This bonding is common in alkali metal and early transition metal α-picolyl complexes and is intermediate between an η^2-alkyl-amine and an η^1-amido-olefin (Figure 2).[8,15] The η^3-(C,C,N)-aza-allylic bonding of the picolyl fragment in 5.2 is also supported by the alternating C-C bonds in the pyridine ring (Table I), the weak Y(1)-C(6) interaction (2.632(5) Å, $^1J_{Y\text{-}C}$ = 6 Hz) and short Y(1)-N(1) (2.389(3) Å) and C(5)-C(6) (1.420(7) Å) bonds.

5-3. Reactivity of Bis(alkoxysilylamido) Yttrium Pyridyl, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-2-$NC_5H_4)$ (5.1), and α-Picolyl, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-$CH_2$-2-$NC_5H_4)$ (5.2), Compounds.

Yttrium and zirconium pyridyl, $Cp^*_2Y(\eta^2$-(C,N)-2-$NC_5H_4)^2$ and $[Cp_2Zr(\eta^2$-(C,N)-2-NC_5H_3-6-$R]^+$ (R = H, Me),[4,6] and zirconium α-picolyl, $[Cp_2Zr(\eta^2$-(C,N)-C(H)Me-2-NC_5H_3-6-Et)$]^+$,[4,7] derivatives are known for their diverse chemistry which ranges from simple complexation of Lewis bases to catalytic alkylation of pyridine. With the corresponding bis(alkoxysilylamido) yttrium pyridyl (5.1) and α-picolyl (5.2) derivatives available, we decided to explore their reactivity towards dihydrogen and unsaturated substrates. The choice of substrates was limited to those earlier empoyed to investigate the reactivity of the corresponding permethylated yttrocene and cationic zirconocene pyridyl and α-picolyl complexes. As complicated reaction patterns were anticipated, it was also decided to perform exploratory NMR tube studies prior to any preparative scale reactions.

Reactivity of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-2-$NC_5H_4)$ (5.1) Towards Dihydrogen. With dihydrogen (4 atm., 65°C), the pyridyl compound 5.1 yields the 1,2-insertion product, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$-$NC_5H_6$ (5.5), analogous to the hydrides $\{[C_6H_5C(NSiMe_3)_2]_2Y(\mu$-H)$\}_2$ (2.9, Chapter 3) and $\{[C_5H_4R]_2Y(\mu$-H)$\}_2$ (R = H, Me).[14b] This strongly suggests that the reaction consists of hydrogenolysis of the pyridyl derivative 5.1, followed by 1,2-insertion (eq. 1) This reaction is comparable to the Ziegler alkylation of pyridines by alkyllithium reagents, for which similar 1,2-insertion products have been observed as intermediates.[16]

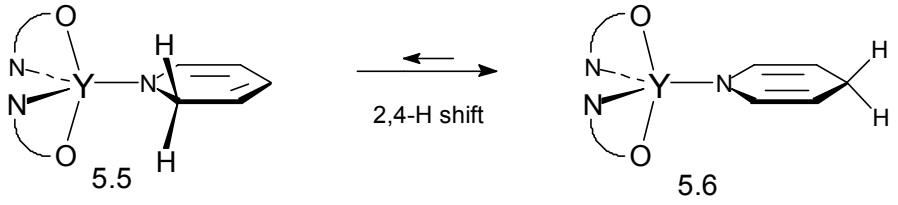


5.1 5.5 (1)

Upon heating (hours, 65°C), compound 5.5 rearranges to the 1,4-isomer (5.6; eq. 2). A similar rearrangement was observed for the 1,2-inserted analogue, $[C_5H_4Me]_2Y$-NC_5H_6,[14b] yielding the 1,4-isomer at room temperature. Direct formation of the 1,4-insertion product has not been

observed, excluding nucleophilic attack at the para-position of pyridine (vide infra). Probably, the ortho proton undergoes an intramolecular 1,3-H shift, comparable to the 1,3-H shift observed during the reactions of $[C_6H_5C(NSiMe_3)_2]_2YR$ (Chapter 3) and $[Me_2Si(NCMe_3)(OCMe_3)]_2YR$ (vide infra) complexes with nitriles. For $\{Cp^*_2Y(\mu\text{-}H)\}_2$, the reaction with pyridine strongly depends on the presence of dihydrogen present. In the absence of dihydrogen, C-H bond activation takes place quantitatively affording the pyridyl derivative, $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$. However, in the presence of dihydrogen, the 1,4-insertion product is exclusively formed.[2] The fact that the intermediate 1,2-insertion product could not be observed indicates that the 1,3-H shift, subsequent to insertion, is fast for the bis-Cp* system.[2] Clearly, the additional dihydrogen present suppresses C-H bond activation in the bis(pentamethyl-cyclopentadienyl) system.

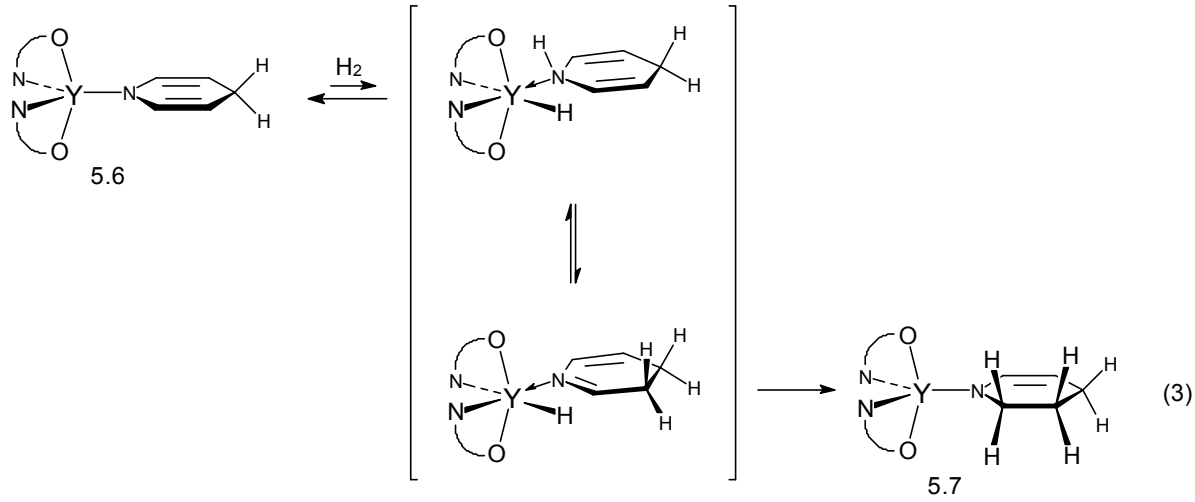
When compound 5.1 was treated with deuterium, build-in of deuterium was observed at both the ortho and para positions, but hardly at the meta position. This indicates that both hydrogenolysis of 5.1 and isomerization of 5.5 into 5.6 are reversible. The absence of deuterium at the meta positions is in agreement with the proposed mechanisms (eq. 1, 2).



(2)

When more than one equivalent of dihydrogen is present, 5.6 is not the final product of the reaction. In the presence of excess dihydrogen, subsequent hydrogenation of one of the double bonds in 5.6 is observed, affording the hydrogenated product 5.7 (24 hours at 65°C, 50 % yield, eq. 3).[17] Assuming that this hydrogenation is a mono-nuclear process, hydrogenolysis of the Y-N bond in 5.6 is most likely. Although hydrogenolysis of an Ln-N bond (Ln = Sc, Y, lanthanide) is not expected to be facile, it has been proposed as one of the crucial steps in the scandium-catalyzed hydrogenation of nitriles.[18] Furthermore, insertion of olefins into Ln-N bonds (Ln-C and Ln-H bond dissociation enthalpies are comparable[19]) is involved during the catalytic hydroamination-cyclization of amino-olefins and amino-alkynes.[20] Hydrogenolysis of 5.6 will give an intermediate hydride enamine adduct (eq. 3). Subsequent enamine-imine

tautomerism will afford the N=C double bond necessary for 1,2-insertion of the intermediate hydride to yield 5.7 (eq. 3). If this proposed mechanism is correct, competitive hydrogenolysis of the alkoxysilylamido ligands should be taken into account. It is not clear though, if the $Me_2Si(N(H)CMe_3)(OCMe_3)$ present (15 %) after 21 hours at 65°C is formed by thermolysis or hydrogenation.



(3)

Although feasible according to the proposed mechanism, hydrogenation of the final double bond in 5.7 was not observed. Heating of reaction mixtures containing 5.7 in the presence of dihydrogen (4 atm.) for prolonged periods of time (days, 65°C) exclusively resulted in thermolysis of 5.7 (^{1}H NMR).

A vanadium-catalyzed, partial reduction of pyridine, very similar to the reaction described here, has recently been reported by Gambarotta et al.[21] Reaction of $[(Me_3Si)_2N]V[\eta^2$-(C,N)-$N(SiMe_3)Si(Me_2)CH_2]$ with pyridine, in the presence of dihydrogen, resulted in partial hydrogenation, giving the vanadium analogue of 5.7, $[(Me_3Si)_2N]_2V$-NC_5H_8. The inability of $[(Me_3Si)_2N]_2V$-NC_5H_8 to undergo further hydrogenation was assigned to the stabilizing (charge delocalization) effect of the final double bond.

Kinetic Study of Hydrogenation of 5.1. The sequential hydrogenation of the pyridyl complex 5.1 was selective enough to be studied in some detail. A conversion versus time plot is shown in Figure 3. Besides 5.1 and the products formed during the hydrogenation of 5.1, the

protolyzed alkoxysilylamido ligand $Me_2Si(N(H)CMe_3)(OCMe_3)$ was the only other compound present in detectable amounts during the reaction.

The first step of the reaction involves formation of the intermediate hydride pyridine adduct. This then undergoes insertion yielding 5.5 (eq. 1). Since no signals in the ^1H NMR spectra taken during the reaction were assignable to intermediate hydrido species, a steady-state approximation can be applied with hydrogenolysis of 5.1 being rate limiting.[22] This is in agreement with the observed instantaneous insertion of pyridine with yttrium hydrides[2,14b] and the much slower hydrogenolysis of yttrium carbyls.[23] When $d[H_2]/dt$ is considered to be zero (a 10 fold excess of H_2 was used), the first step of the reaction (eq. 1) becomes first-order in [5.1] and zero-order in dihydrogen.[22] The conversion of 5.1 into 5.5 does indeed show clean first-order dependence on 5.1 ($k = 1.1(\pm 0.1)\cdot10^{-2}$ L·mol^{-1}·s^{-1}, $\Delta G^{\ddagger}_{(338K)} = 95.8(\pm 0.1)$ kJ·mol^{-1}).

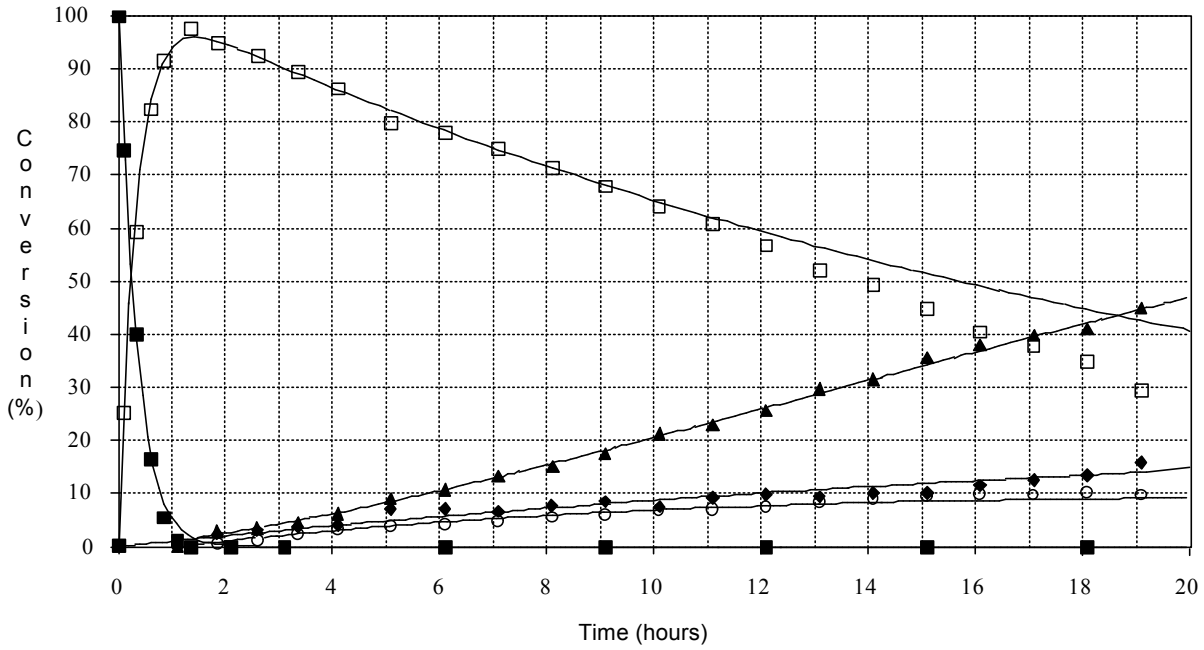


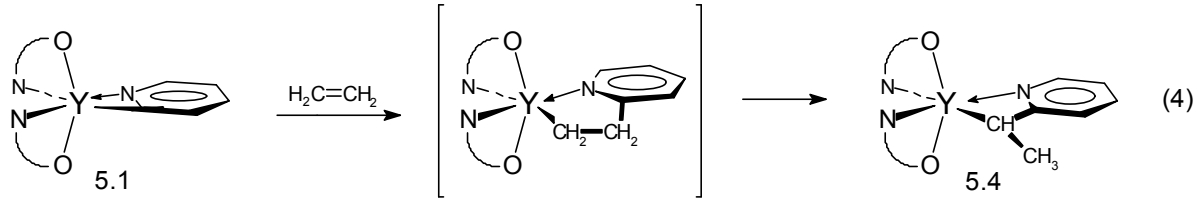
Figure 3.Conversion versus time plot of the hydrogenation of 5.1 at 65°C. ■ = 5.1, □ = 5.5, ○ = 5.6, ▲ = 5.7, ◆ = $Me_2Si(N(H)CMe_3)(OCMe_3)$.

The concentration of 5.5 is dependent on both the rate of the preceding hydrogenation of 5.1 and the rate of the subsequent isomerization of 5.5 into 5.6. Hence, the reaction is expected to be first-order in both 5.1 and 5.6. When inserting the rate constant for hydrogenation of 5.1 into the rate expression for the isomerization of 5.5 (see appendix), the rate constant for the isomerization ($k = 1.3(\pm 0.2)\cdot10^{-5}$ s^{-1}, $\Delta G^{\ddagger}_{(338K)} = 114.5(\pm 0.2)$ kJ·mol^{-1}) can directly be

derived.[22] As can be seen from Figure 3, the theoretical curve for the formation of 5.5 corresponds well with the data points for the first 10 hours. After 10 hours, the curve starts to deviate from the data points as the calculation does not account for the formation of $Me_2Si(N(H)CMe_3)(OCMe_3)$ (9 % after 10 hours, vide infra). For the final step (eq. 3), the same assumptions as for the hydrogenation of 5.1 were made. Since hydrogenolysis of Y-N bonds is expected to be more difficult than that of Y-C bonds, it is reasonable to assume that hydrogenolysis of 5.6 is rate limiting, which is supported by the absence of hydrido intermediates (^{1}H NMR). The concentration of 5.6 does not extend above 9 % throughout the reaction. Therefore, the rate constant of the final hydrogenation step was derived from the increase in 5.7 concentration. To simplify the theoretical rate expression, the data points collected after 1.4 hours, when all 5.1 has been consumed (d[5.1]/dt = 0), were used. Using the rate constants for the hydrogenation of 5.1 and the isomerization of 5.5, a curve was obtained which corresponds very well with the experimental data ($k = 5.3(\pm 0.2)\cdot10^{-4}$ l·mol^{-1}·s^{-1}, $\Delta G^{\ddagger}_{(338K)} = 104.3(\pm 0.2)$ kJ·mol^{-1}).

Although some assumptions had to be made to be able to calculate the rate constants (see Appendix for details), the observed kinetics for all the individual steps are in good agreement with the proposed mechanism (eq. 1 - 3, appendix). Since only for the isomerization of 5.5 into 5.6 a detectable deviation between the theoretical curve and the data points was observed after 10 hours, we assume that the main source for $Me_2Si(N(H)CMe_3)(OCMe_3)$ is 5.5. However, it is not clear whether the $Me_2Si(N(H)CMe_3)(OCMe_3)$ is formed by thermolysis or by competitive hydrogenolysis. As the amount was limited to 15 % after 21 hours, this side-reaction was ignored.

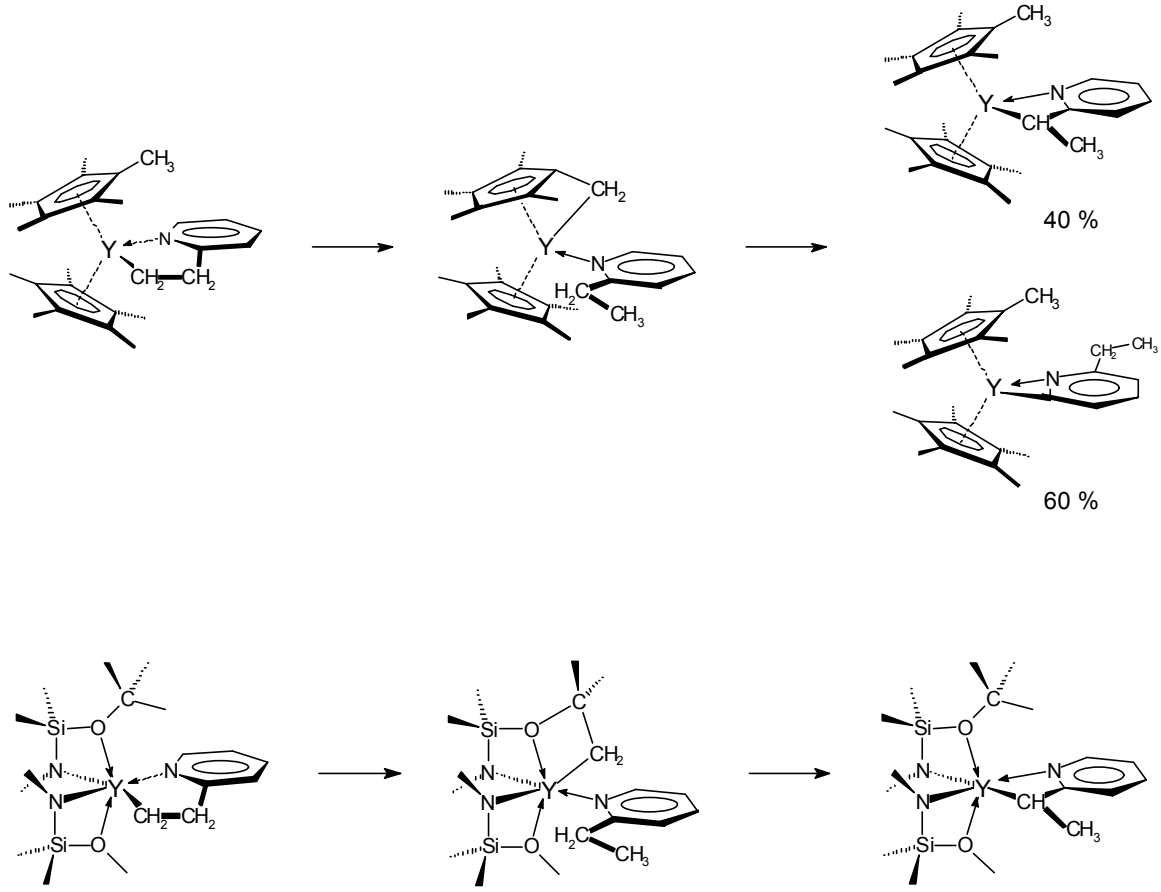
Reactivity Towards Ethylene. With excess ethylene, 5.1 reacts slowly (65 h, 50°C) to form the insertion product, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}C(H)Me\text{-}2\text{-}NC_5H_4)$ (5.4, eq. 4) in 36 % yield.



(4)

The reaction is not clean and the presence of substantial amounts of $Me_2Si(N(H)CMe_3)(OCMe_3)$, 2-ethyl-pyridine and isobutene indicates that disproportionation and thermolysis of the various compounds has occurred. Nevertheless, the reaction product (5.4) could clearly be identified by ^1H NMR spectroscopy. The expected 1,2-insertion product $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2CH_2\text{-}2\text{-}NC_5H_4)$ (eq. 4) was not observed. Probably, it rearranges quickly into 5.4 under the conditions applied. Comparable observations have been made for the reaction of $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_4)$ with ethylene. Initially, the 1,2-insertion product $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}CH_2CH_2\text{-}2\text{-}NC_5H_4)$ was formed which, upon heating, slowly rearranged into a mixture of $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Et)$ and $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}(C(H)Me\text{-}2\text{-}NC_5H_4)$. For this isomerization reaction, Deelman et al.[2] proposed an intermediate fulvene species, $Cp^*(\sigma,\eta^5\text{-}CH_2C_5Me_4)Y$, which subsequently metalates 2-ethyl-pyridine in both the benzylic and the ortho positions (Scheme 3).

Scheme 3.

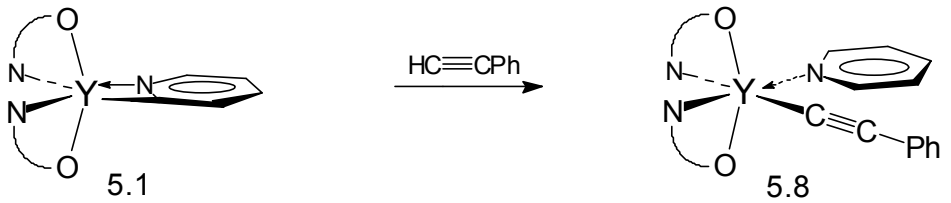


In a similar manner, metalation of one of the tert-butyl groups (either $OCMe_3$ or $NCMe_3$) of the alkoxysilylamido ligands may generate an intermediate $[Me_2Si(NCMe_3)(OCMe_3)][\eta^3$-$(C,N,O)$-$Me_2Si(NCMe_2(CH_2))(OCMe_3)]Y.EtPy$ or $[Me_2Si(NCMe_3)(OCMe_3)][\eta^3$-$(C,N,O)$-$Me_2Si(NCMe_3)(OCMe_2(CH_2))]Y.EtPy$ species. This intermediate may subsequently metalate the released ethylpyridine at the benzylic position, forming 5.4. Evidence for such an intermediate is obtained from the thermolysis of $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ (4.6), for which metalation of the alkoxysilylamido ligands, followed by elimination of isobutene was observed (Chapter 4).

In analogy with the earlier reported catalytic conversion of pyridine into 2-ethyl-pyridine by $Cp^*_2Y(\eta^2$-(C,N)-2-$NC_5H_4)$,[2] 5.1 was treated with excess ethylene and pyridine (65°C). However, no catalytic pyridine alkylation could be observed and the reaction stops after formation of 5.4. The remaining excess of ethylene and pyridine was left unreacted. Heating (70°C) of the reaction mixture for prolonged periods of time, resulted in thermal decomposition of 5.4 ($Me_2Si(N(H)CMe_3)(OCMe_3)$, 2-ethyl-pyridine and isobutene were formed).

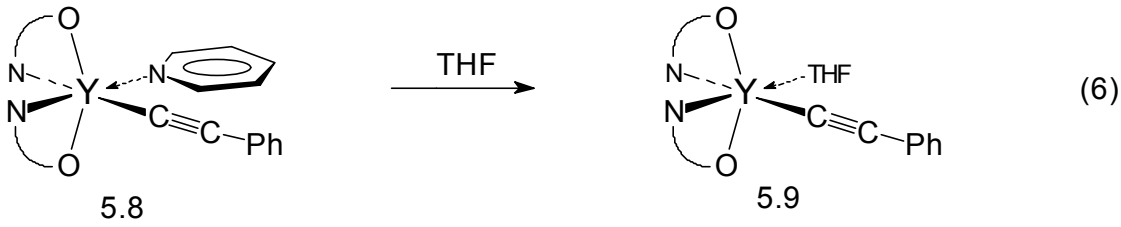
As expected on the basis of the results described above, the picolyl complex 5.2 did not react with ethylene. Heating (days, 65°C) of an NMR tube containing 5.2 in the presence of ethylene (4 atm.) exclusively resulted in the thermal decomposition of 5.2; no ethylene consumption could be observed.

Reactivity Towards 1-Alkynes. To assess how the the carbyl group influences the reactivity of the complexes, the reaction of 5.1 with HC≡CPh was carried out. It was assumed that the combination of smaller steric bulk and the ring strain in the pyridyl fragment of 5.1, compared with the $CH(SiMe_3)_2$ group in 4.6, would increase the distinction between the reactivity of the carbyl group and the ancillary ligands.

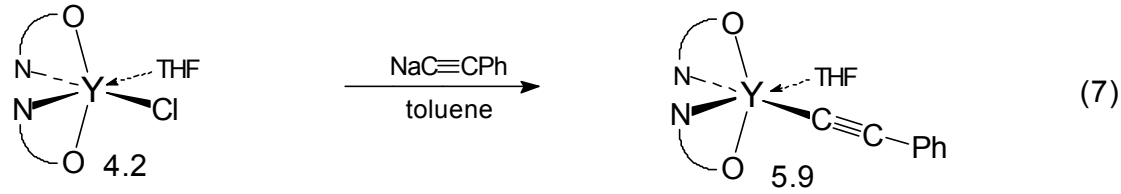


5.1 5.8 (5)

Although leaving much to be desired, a significant increase in selectivity could indeed be observed. Whereas the alkyl complex 4.6 reacts completely aselective with one equivalent of HC≡CR (R = Ph, $SiMe_3$, CMe_3), liberating 65 % of $Me_2Si(N(H)CMe_3)(OCMe_3)$ (Chapter 4), reaction of 5.1 with one equivalent of HC≡CPh resulted in only partial protolysis of the alkoxysilylamido ligands (37 % $Me_2Si(N(H)CMe_3)(OCMe_3)$ formed) and afforded the alkynyl complex, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$-C≡CPh.Py (5.8, eq. 5), in 51 % yield (NMR). With 3 equivalents of HC≡CPh, protolysis of both the pyridyl and alkoxysilylamido ligands was observed, analogous to 4.6. Leaving the competitive protolysis of the ancillary ligands out of consideration, the reaction of 5.1 with HC≡CPh is similar to that of $Cp^*_2Y(\eta^2$-(C,N)-2-$NC_5H_4)$ with HC≡CR (R = H, Me), which afforded the corresponding acetylide pyridine adducts, Cp^*_2Y-C≡CR.Py.[2] In contrast, $[Cp_2Zr(\eta^2$-(C,N)-2-NC_5H_3-6-Me)$]^+$ and $[Cp_2Zr(\eta^2$-(C,N)-CH_2-2-NC_5H_3-6-Me)$]^+$ gave insertion with terminal alkynes,[6c] which clearly indicates the difference in character of the Y-C and Zr-C bonds.



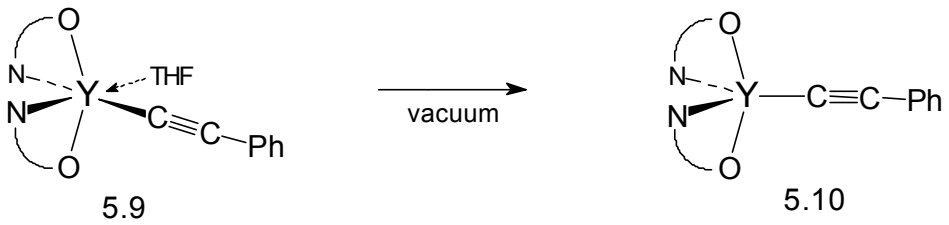
(6)



(7)

The extreme solubility of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$C≡CPh.Py (5.8) hampered its purification and isolation dramatically. While attempts to remove the coordinated pyridine (stripping with toluene, sublimation) failed, the pyridine could easily be replaced by THF yielding the adduct, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$C≡CPh.THF (5.9, eq. 6). The acetylide 5.9 could also be synthesized directly by chloride metathesis of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$Cl.THF (4.2) with NaC≡CPh (eq. 7). The solubility of compound

5.9 was sufficiently low to allow recrystallization and isolation from n-pentane. Unfortunately, crystals of 5.9 readily lost n-pentane from the crystal lattice. While stable enough to obtain an X-ray structure determination, the n-pentane had to be removed to obtain a stisfactory elemental analysis. Therefore, 5.9 was stripped with toluene and dried in vacuo. Surprisingly, not only the n-pentane but the coordinated THF was removed as well (eq. 8). Interestingly, the ^{13}C NMR spectrum of the compound formed is identical to that of 5.9 with the only exception that some of the resonances are slightly shifted. The doublet resonance for the α-C of 5.10 (δ = 144.2 ppm, $^{1}J_{Y\text{-}C}$ = 60 Hz; cf.: 5.9(α-C): δ = 145.3 ppm, $^{1}J_{Y\text{-}C}$ = 53 Hz) excludes a dimeric structure with bridging alkynyl fragments, as often found in organoyttrium and lanthanide chemistry. For such complexes, the resonances of the α-carbons appear as triplets ($^{1}J_{Y\text{-}C}$ ~ 20 Hz), due to the coupling of two (time-averaged) identical yttrium atoms. Probably, the steric bulk of the alkoxysilylamido ligands (larger than that of the bis-Cp* system, Chapter 7) blocks dimerization. Similarly, the steric congestion in $\{Cp^*_2Sm\text{-}C{\equiv}CCMe_3\}_2$ precluded bridging of the alkynyl fragments and the monomeric units are stabilized by a peculiar agostic interaction of a Cp*-methyl group of an adjacent molecule. Unfortunately, compound 5.10 crystallizes as thin needles, unsuitable for X-ray analysis.



5.9 5.10 (8)

Compared to other bis(alkoxysilylamido) yttrium carbyl complexes (4.6, 5.1 - 5.4), the unsolvated acetylide 5.10 is thermally remarkably stable and shows no decomposition in benzene after several days at 100°C. No evidence for C-C coupling yielding μ-trienediyl species, as formed upon heating of $\{Cp^*_2Ln\text{-}C{\equiv}CR\}_n$ (Ln = La, R = Ph, CMe_3; Ln = Ce, R = Me, CMe_3; Ln = Sm, R = Ph, CH_2CH_2Ph, $CH_2CH_2CHMe_2$),[24] was observed either. Probably, the steric bulk of the ligand system in 5.10, which prevents dimerization also blocks C-C coupling of the acetylide fragments.

Molecular Structure of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y\text{-}C{\equiv}CPh.THF$ (5.9). A low temperature X-ray diffraction study of 5.9 was performed and notable features are reported below.[25] A PLUTO drawing of 5.9 is shown in Figure 4 and selected bond distances and angles listed in Table II. The n-pentane in the crystal lattice is left out of consideration. The molecule is a monomer, formed by a distorted octahedral yttrium atom coordinated by two alkoxysilylamido ligands, one acetylide fragment and one THF molecule.

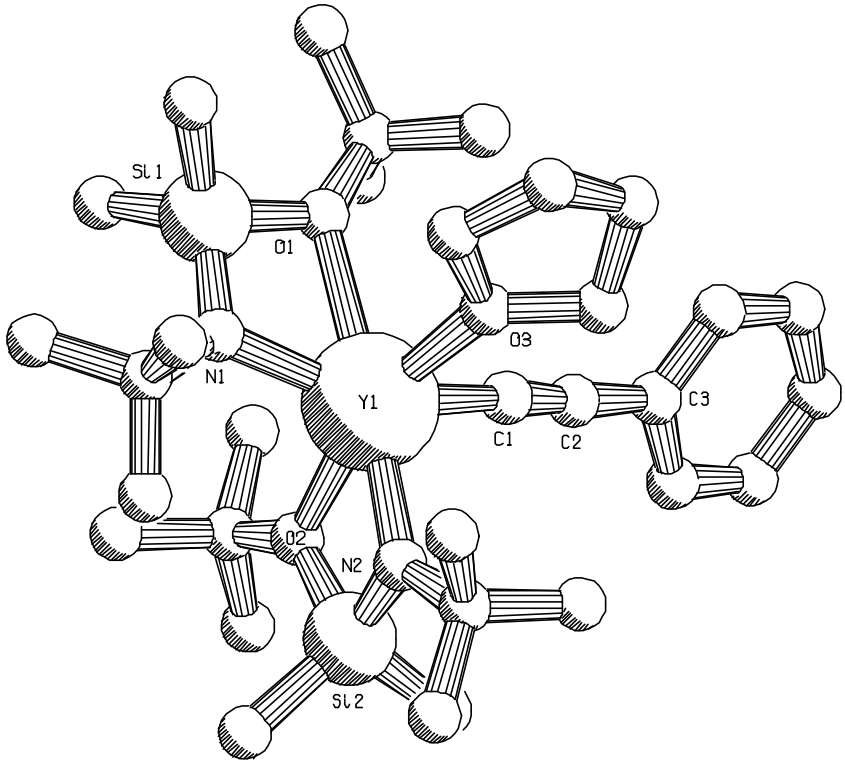


Figure 4 PLUTO drawing of the molecular structure of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y\text{-}C{\equiv}CPh.THF$ (5.9). Hydrogens and the n-pentane are omitted for clarity.

In the pseudo-trigonal-pyramidal coordinated complexes 4.6 and 5.2 both alkoxysilylamido nitrogens are equatorially located. In 5.9 one of the nitrogens is in equatorial position, trans to the acetylide group, whereas the other is axial. Since the same orientation of the alkoxysilylamido ligands was observed in $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\mu\text{-}(N,N')\text{-}N(H)\text{-}C(Me){=}C(H)\text{-}C{\equiv}N)\}_2$ (4.10, Chapter 4) and $[Me_2Si(NCMe_3)(OCMe_3)]_2Yb(\mu\text{-}Cl)_2Li.THF_2$,[10] this seems to be the most favorable conformation in octahedral complexes. With torsion angles N(1)-Y(1)-O(1)-Si(1) and N(2)-Y(1)-O(2)-Si(2) of -3.63(10)^o and -5.67(11)^o respectively, both alkoxysilylamido ligands form almost planar rings with yttrium. The Y(1)-N(1) (2.279(3) Å) and

Y(1)-N(2) (2.266(3) Å) bonds are within the range normal for Y-N σ-bonds in bis(N,O-bis(tert-butyl)alkoxydimethylsilylamido) yttrium derivatives (4.6, 4.10, 5.2) and indicate substantial π-interaction of the nitrogen lone-pairs with the yttrium. Whereas the Y(1)-O(2) (2.375(2) Å) and Y(1)-O(3) (2.378(2) Å) bond distances are normal Y←:O dative bonds,[12] the Y(1)-O(1) (2.571(2) Å) bond is significantly longer. The Y(1)-C(1) (2.448(4) Å) distance is very similar to the yttrium-carbon bonds in [p-MeO-C_6H_4C($NSiMe_3$)$_2$]$_2$YCH($SiMe_3$)$_2$ (2.8_{OMe}, 2.431(5) Å, Chapter 2), Cp*$_2$YMe.THF (2.44(2) Å)[26] and Cp*$_2$YCH($SiMe_3$)$_2$ (2.446(7) Å),[11] respectively. This is unusual since metal-alkynyl bonds are generally shorter than corresponding metal-alkyl bonds.[13c] Interestingly, a comparable long metal-alkynyl bond has been observed in the closely related Cp*$_2$Sm-C≡CPh.THF complex.[27] Whereas in the samarium compound, the long Sm-C bond was accompanied by a short C≡C bond (C≡$C_{av.}$: 1.12(2) Å), the C≡C bond in 5.9 of 1.217(5) Å is normal for non-bridging alkynyl groups.[28]

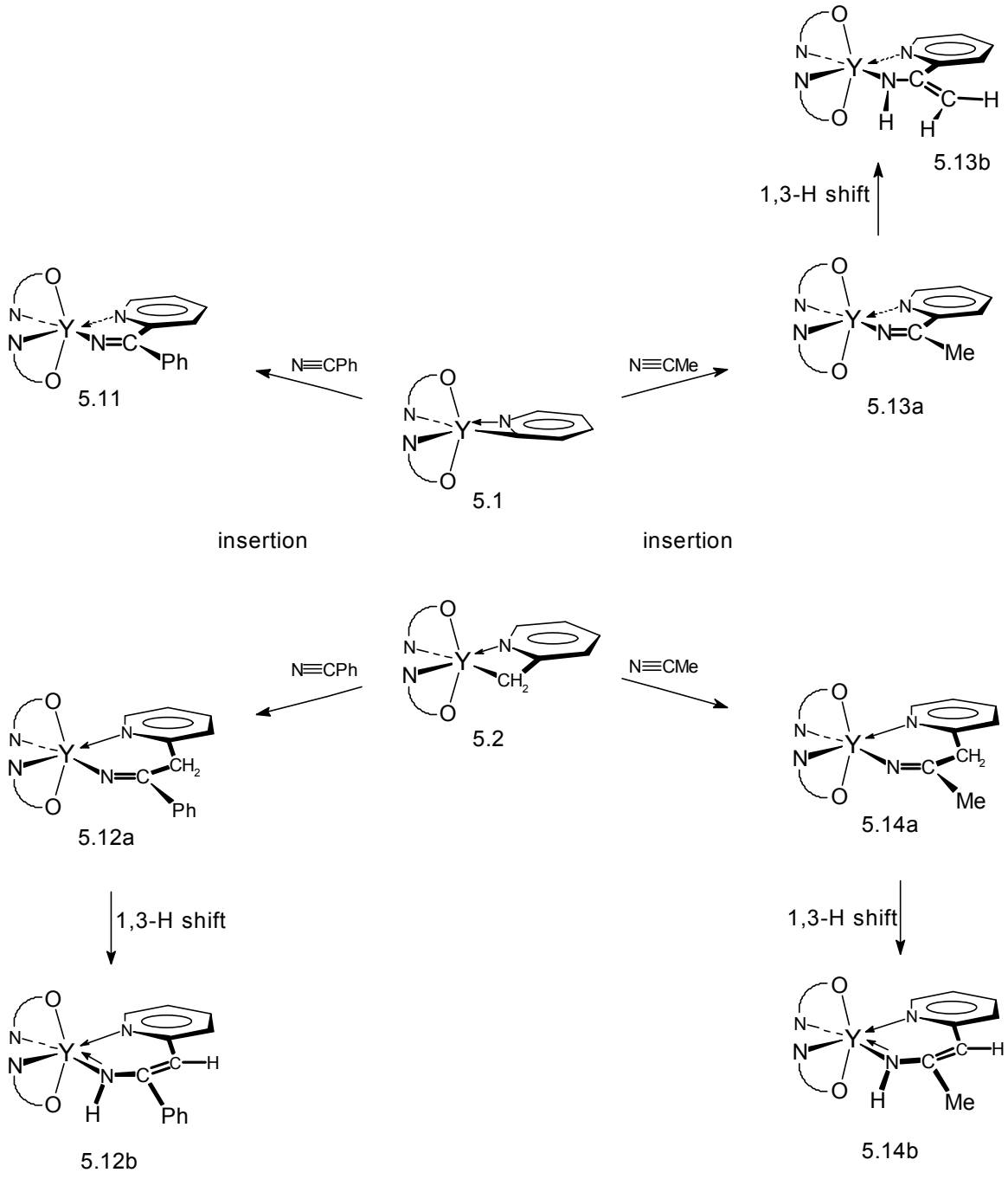
Table II. Selected Bond Distances and Angles for [$Me_2Si(NCMe_3)(OCMe_3)$]$_2$Y-C≡CPh.THF (5.9).

Distances (Å)		Angles (deg.)	
Y(1)-N(1)	2.279(3)	Si(1)-Y(1)-Si(2)	133.00(3)
Y(1)-N(2)	2.266(3)	N(1)-Y(1)-O(1)	62.22(9)
Y(1)-O(1)	2.571(2)	N(2)-Y(2)-O(2)	65.36(9)
Y(1)-O(2)	2.375(2)	N(2)-Y(1)-O(1)	173.47(9)
Y(1)-O(3)	2.378(2)	N(1)-Y(1)-O(2)	97.25(9)
Y(1)-C(1)	2.448(4)	C(1)-Y(1)-O(3)	87.67(10)
C(1)-C(2)	1.217(5)	O(1)-Y(1)-C(1)	87.78(10)
C(2)-C(3)	1.444(5)	O(2)-Y(1)-C(1)	85.15(11)
		O(1)-Y(1)-O(3)	80.85(8)
		N(2)-Y(1)-O(3)	98.37(10)
		N(1)-Y(1)-C(1)	147.69(11)
		N(1)-Y(1)-O(3)	98.28(9)
		O(2)-Y(1)-O(3)	160.87(8)

Reactivity Towards Nitriles. Group 3 metal and lanthanide alkyl and hydrido complexes, $\{[C_5H_4R]_2Y(\mu\text{-}H).THF\}_2$, (R = H, Me),[29] Cp^*_2LnR (Ln = Sc, R = C_6H_4-4-Me, H; Ln = Y, La, Ce, R = $CH(SiMe_3)_2$), [18,29b] and $[C_6H_5C(NSiMe_3)_2]_2YR$ (R = CH_2Ph,THF (2.7), $CH(SiMe_3)_2$ (2.8), μ-H (2.9), Chapter 3), react smoothly with nitriles. Depending on the metal complex and nitrile applied, either insertion or C-H bond activation is observed.

The reactions of 5.1 and 5.2 with benzonitrile and acetonitrile (N≡CR, R = Ph, Me), are summarized in Scheme 4. The reactivity of both complexes is dominated by insertion and, when possible, subsequent 1,3-H shift. Generally, the reactions are fast at room temperature and the products are formed in high yield. The extremely high solubility of the complexes presented in Scheme 4 dramatically hampered their purification. Only 5.13b and 5.14b could be isolated as analytically pure crystals. However, all the compounds could unequivocally be identified by ^1H and ^{13}C NMR spectroscopy.

Scheme 4.



With benzonitrile, 5.1 gave straightforward insertion affording $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N{=}C(Ph)\text{-}2\text{-}NC_5H_4)$ (5.11). Similarly, the picolyl compound 5.2 inserts benzonitrile, but the initially formed $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N{=}C(Ph)CH_2\text{-}2\text{-}NC_5H_4)$ (5.12a) rearranges by 1,3-hydrogen shift to the corresponding enamine complex, $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2\text{-}(N,N')\text{-}N(H)\text{-}C(Ph){=}C(H)\text{-}2\text{-}NC_5H_4)$ (5.12b). A similar reaction was observed for $[C_6H_5C(NSiMe_3)_2]_2YCH_2Ph.THF$ with $N{\equiv}CCMe_3$ (Chapter 3). With acetonitrile, either C-H bond activation or insertion may occur. As discussed

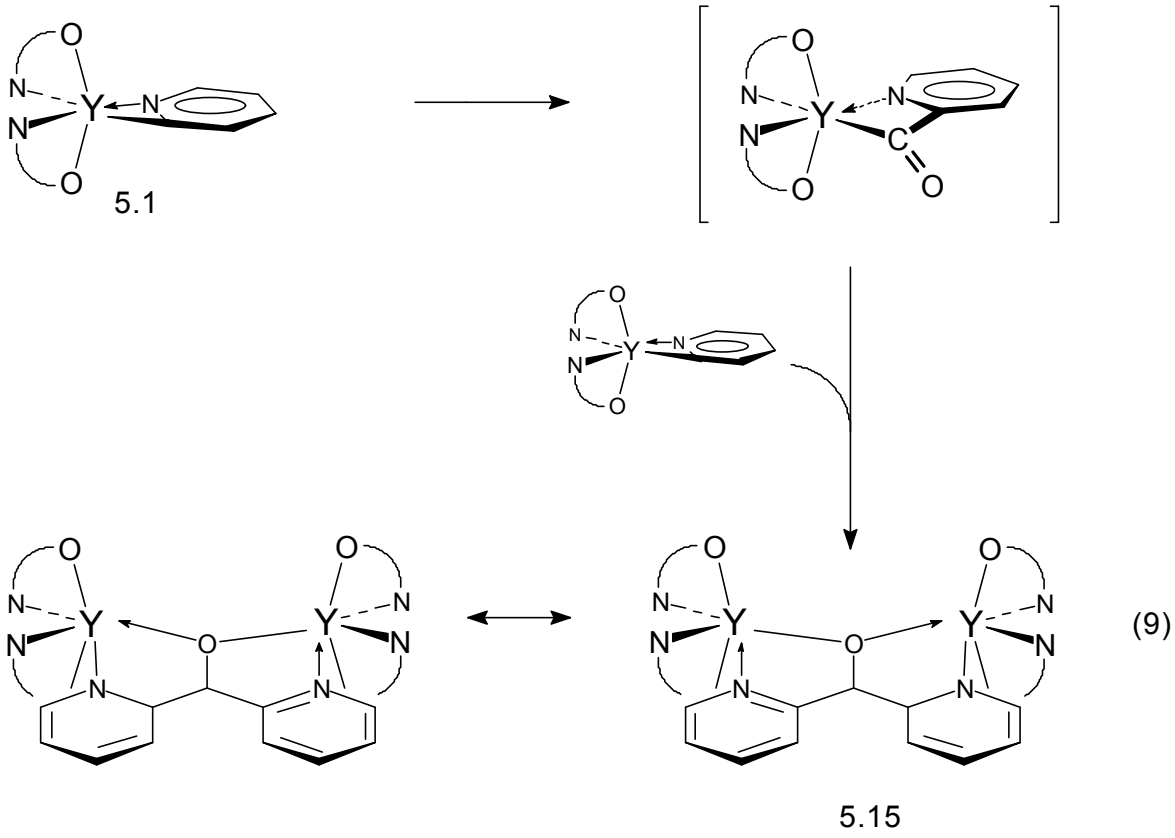
in Chapter 3 and 4, the reaction strongly depends on the character of the alkyl (or hydrido) group. Hence, N≡CMe is a useful substrate to probe the metal carbon bond character. Compound 5.1 reacts instantaneously with N≡CMe, initially yielding $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N=C(Me)-2-$NC_5H_4)$ (5.13a). This complex is not stable and rearranges at room temperature by 1,3-H shift into $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N(H)-C(=$CH_2$)-2-$NC_5H_4)$ (5.13b). Similar to the reaction with benzonitrile, reaction of 5.2 with acetonitrile afforded $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N(H)-C(Me)=C(H)-2-$NC_5H_4)$ (5.14b). The reaction is very fast at room temperature. Although $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N=C(Me)$CH_2$-2-$NC_5H_4)$ (5.14a) could not be observed in the ^{1}H NMR spectra taken during the reaction, it is likely that it is formed as an intermediate which rearranges quickly into 5.14b (Scheme 4). With the CH_3 resonance at δ 1.94 ppm, the vinylic proton as a doublet at δ 5.02 ppm ($^4J_{HH}$ = 2.1 Hz) and the NH as a broad singlet at δ 6.23 ppm, the ^{1}H NMR spectrum of 5.14b corresponds well with that of $[Cp_2Zr(\eta^2$-(N,N')-N(H)-C(Me)=C(H)-2-NC_5H_3-6-Me)$]^+$, formed by reaction of $[Cp_2Zr(\eta^2$-(C,N)-CH_2-2-NC_5H_3-6-Me)$]^+$ with acetonitrile.[7]

The observation that both 5.1 and 5.2 give insertion of acetonitrile demonstrates that the pyridyl and picolyl groups are less Brønsted basic than the $CH(SiMe_3)_2$ group in $Cp^*_2LnCH(SiMe_3)_2$ (Ln = La, Ce),[29b] $[C_6H_5C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (2.8, Chapter 3) and in $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ (4.6, Chapter 4) for which C-H bond activation is observed. Although 5.2 and $[C_6H_5C(NSiMe_3)_2]_2YCH_2Ph.THF$ (2.7) are closely related, the reactivity towards acetonitrile is different. Whereas for 5.2 exclusively insertion is observed, the bis(benzamidinato) yttrium benzyl complex (2.7) also shows a minor tendency for C-H bond activation, yielding a mixture of metalation (3.10, 10 %) and insertion (3.11a, 50 %; 3.11b, 40 %) products (Chapter 3). Hence, even small differences in the character of the M-C bond may result in a different reaction pattern.

As observed during the reaction of 5.2 with N≡CR (R = Ph, Me) and the corresponding reactions of 2.7, 2.8 (Chapter 3), 4.6 (Chapter 4), and $[Cp_2Zr(\eta^2$-(C,N)-CH_2-2-NC_5H_3-6-Me)$]^+$ with N≡CMe,[7] 1,3-H shift appears to be a common process to increase the stability of these complexes.

Reactivity Towards Carbon Monoxide. Group 3 and lanthanide carbyl complexes are known to react with CO under formation of unstable η^2-acyl compounds which either rearrange to enolates or form dinuclear enedione diolate derivatives.[30] Deelman[2] reported the

formation of a novel μ,η^2,η^2-dipyridylketone derivative upon treatment of $Cp^*_2Y(\eta^2$-(C,N)-2-$NC_5H_4)$ with CO.



5.1

5.15

(9)

This reaction clearly demonstrates the ability of pyridyl fragments to stabilize otherwise unstable functionalities. In order to compare the pyridyl group in 5.1 with that in $Cp^*_2Y(\eta^2$-(C,N)-2-$NC_5H_4)$, reaction with CO was carried out. Treatment of 5.1 in benzene with excess CO, resulted in the intensely blue compound, $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y\}\{\mu,\eta^2,\eta^2$-(N,N',O)-$OC(2\text{-}NC_5H_4)_2\}$ (5.15, eq. 9), analogous to the permethylated yttrocene derivative, $\{Cp^*_2Y\}_2\{\mu,\eta^2,\eta^2$-(N,N',O)-$OC(2\text{-}NC_5H_4)_2\}$.[2] Both the ^{13}C NMR resonance (δ = 147.3 ppm) and the IR absorption ($\nu_{C=O}$ = 1404 cm^{-1}) of 5.15 indicate that the carbonyl functionality is significantly reduced.[30b,31] These spectral data are nearly identical to those for the structurally characterized $\{Cp^*_2Y\}_2\{\mu,\eta^2,\eta^2$-(N,N',O)-$OC(2\text{-}NC_5H_4)_2\}$.[2]

As proposed by Deelman, the formation of 5.15 is thought to proceed by CO insertion followed by nucleophilic attack of an other equivalent of 5.1 and is schematically presented in

eq. 9. A more detailed discussion concerning the bonding of the μ,η^2,η^2-dipyridylketone fragment is given elsewhere.[2]

5-4. Concluding Remarks.

In is clear that the bis(N,O-bis(tert-butyl)alkoxydimethylsilylamido) ligand environment can stabilize yttrium alkyl and aryl complexes. For catalytic applications, however, the bis(alkoxysilylamido) yttrium complexes studied here are not suitable since the ligand system is not inert. The high Brønsted basicity of the amido functionality, in combination with the poor coordinating ability of the ether function results in protonation or exchange (leading to disproportionation) of the alkoxysilylamido ligands. Furthermore, when temperatures higher than 60^{o}C are required, metalation of the alkoxysilylamido tert-butyl substituents, comparable to fulvene formation in the bis-Cp* system, takes place.

Interestingly, when substrates containing acidic protons and high temperatures are avoided, the bis(alkoxysilylamido) yttrium pyridyl and picolyl complexes 5.1 and 5.2, display a reactivity very similar to that of the corresponding permethylated yttrocene pyridyl, $Cp^*_2Y(\eta^2\text{-}(C,N)\text{-}NC_5H_4)$, cationic zirconocene pyridyl $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}NC_5H_3\text{-}6\text{-}R)]^+$ (R = H, Me), and picolyl $[Cp_2Zr(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_3\text{-}6\text{-}R)]^+$ (R = Me, Et) complexes. Furthermore, as the hydrogenation of 5.1 demonstrates, changing the properties of the metal center by altering the ligand environment, may result in previously unknown reactivity.

As will be discussed in more detail in Capter 7, the bis(N,O-bis(tert-butyl)alkoxydimethylsilylamido) ligand environment is sterically more demanding than the bis(cyclopentadienyl), bis(N,N'-bis(trimethylsilyl)benzamidinato) and bis(pentamethyl-cyclopentadienyl) ligand systems. This is clearly illustrated by the monomeric nature of the acetylide, $[Me_2Si(NCMe_3)(OCMe_3)]_2YC{\equiv}CPh$ (5.10). This contrasts the chemistry of the sterically less hindered bis(N,N'-bis(trimethylsilyl)benzamidinato) yttrium acetylides, which is dominated by the tendency to form, very stable dimers.

5-5. Experimental Section.

Materials and Methods. All compounds are extremely oxygen and moisture sensitive. Manipulations were therefore carried out under nitrogen by using glovebox (Braun MB-200) and Schlenk techniques. Hydrogen (Hoekloos 99.9995 %), deuterium (Matheson, C.P.) and ethylene

(DSM Research B.V.) were used as purchased. HC≡CPh, MeC≡N, PhC≡N, pyridine, α-picoline and 2,6-dimethylpyridine (Janssen) were dried over 4 Å molecular sieves and distilled prior to use. Benzene-d_6 was dried over Na/K alloy and distilled prior to use. All solvents were distilled from Na (toluene), K (THF) or Na/K alloy (ether, n-pentane, hexanes) and stored under nitrogen. $[Me_2Si(NCMe_3)(OCMe_3)]_2YCl.THF$ (4.2) and $[Me_2Si(NCMe_3)(OCMe_3)]_2YCH(SiMe_3)_2$ (4.6) were prepared following the procedure described in Chapter 4.

Physical and Analytical Measurements. NMR spectra were recorded on a Varian Gemini-200 (^{1}H: 200 MHz, ^{13}C: 50.3 MHz) or a Varian VXR-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances. IR spectra were recorded on a Mattson-4020 Galaxy FT-IR spectrophotometer. Elemental analyses were carried out at the Analytical Department of this laboratory; given data are the average of at least two independent determinations.

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-$NC_5H_4)$ (5.1). 2-bromopyridine (0.63 mL, 6.61 mmol) was dissolved in ether (40 mL) and cooled to -80°C. Then, n-BuLi (2.67 mL, 2.5 M solution in hexanes, 6.67 mmol) was added. After stirring for 30 minutes, 4.2 (3.97 g, 6.60 mmol) was added to the resulting red solution. The reaction mixture was allowed slowly to warm to room temperature and stirred for 20 hours. The volatiles were removed *in vacuo* and the resulting sticky residue was stripped with n-pentane (3 x 7 mL). Extraction with n-pentane (15 mL), concentration and cooling to -80°C, yielded 5.1 (1.10 g, 1.92 mmol, 29 %) as red-brown crystals. Further concentration of the mother liquor yielded a second crop of 5.1 (0.65 g, 1.13 mmol, 17 %) as a microcrystalline powder upon cooling to -80°C. IR (KBr/Nujol, cm^{-1}) 3081 (w), 3054 (m), 3028 (m), 2728 (w), 1574 (m), 1535 (w), 1429 (m), 1410 (m), 1368 (s), 1354 (m), 1248 (s), 1211 (s), 1181 (s), 1069 (s), 1032 (m), 990 (m), 932 (s), 912 (s), 910 (s), 851 (s), 818 (s), 802 (m), 768 (s), 731 (s), 665 (m), 613 (m), 521 (m), 497 (m), 488 (m), 474 (m), 421 (w). ^{1}H NMR (benzene-d_6, δ): 8.41 (dd, 1H, NC_5H_4(H6), $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 0.9 Hz), 7.96 (dd, 1H, NC_5H_4(H3), $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.07 (td, 1H, NC_5H_4(H4), $^3J_{H-H}$ = 7.5 Hz, $^4J_{H-H}$ = 1.3 Hz), 6.70 (ddd, 1H, NC_5H_4(H5), $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 1.3 Hz), 1.53 (s, 18H, $C(CH_3)_3$), 1.08 (s, 18H, $C(CH_3)_3$), 0.39 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6, δ), 226.0 (d, NC_5H_4(ipso-C), $^1J_{Y-C}$ = 26 Hz), 145.8 (d, NC_5H_4, $^1J_{C-H}$ = 174 Hz), 132.9 (d, NC_5H_4, $^1J_{C-H}$ = 162 Hz), 132.3 (d, NC_5H_4, $^1J_{C-H}$ = 157 Hz), 121.0 (d, NC_5H_4, $^1J_{C-H}$ = 158 Hz), 76.3 (s, $C(CH_3)_3$), 51.9 (s, $C(CH_3)_3$), 37.2 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 124 Hz), 31.4 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 126 Hz), 8.0 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd. (found) for $C_{25}H_{52}N_3O_2Si_2Y$: C, 52.52 (52.19); H, 9.17 (9.04); N, 7.35 (6.97); Y, 15.55 (15.43).

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-$CH_2$-2-$NC_5H_4)$ (5.2). A THF (40 mL) solution of α-picoline (0.7 mL, 7.0 mmol) was treated with n-BuLi (2.8 mL, 2.5 M in hexanes, 7.0 mmol) at -40°C. The red solution was allowed to warm to room temperature and then stirred for 90 minutes. The volatiles were removed *in vacuo* and the residue was dissolved in toluene (80 mL). After cooling to -80°C, 4.2 (4.2 g, 7.0 mmol) was added and the reaction mixture allowed to warm to room temperature. After stirring for 20 minutes, the solvent was evaporated and the crude product stripped

with n-pentane (3 x 15 mL). Then the product was redissolved in n-pentane (30 mL). Filtration, concentration and slow cooling to -30°C yielded 5.2 (2.05 g, 3.5 mmol, 50 %) as rod-shaped orange crystals. IR (KBr/Nujol, cm^{-1}): 1607(s), 1518(w), 1416(m), 1395(w), 1354(m), 1304(m), 1277(w), 1248(s), 1208(s), 1177(s), 1152(w) 1067(s), 1033(w), 991(w), 924(s), 910(s), 849(s), 820(s), 766(s), 733(s), 696(w), 638(w), 613(w), 583(w), 525(w), 498(w). ^{1}H NMR (benzene-d_6, δ): 7.75 (d, 1H, NC_5H_4(H6), $^3J_{H-H}$ = 5.6 Hz), 6.73 (ddd, 1H, NC_5H_4(H4), $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.52 (d, 1H, NC_5H_4(H3), $^3J_{H-H}$ = 8.6 Hz), 5.90 (ddd, 1H, NC_5H_4(H5), $^3J_{H-H}$ = 6.8 Hz, $^3J_{H-H}$ = 5.6 Hz, $^4J_{H-H}$ = 1.3 Hz), 2.73 (d, 2H, Y-CH_2, $^2J_{Y-H}$ = 0.9 Hz), 1.51 (s, 9H, C(CH_3)$_3$), 1.49 (s, 9H, C(CH_3)$_3$), 1.31 (s, 18H, C(CH_3)$_3$), 0.43 (s, 6H, Si(CH_3)$_2$), 0.36 (s, 3H, Si(CH_3)$_2$), 0.32 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ), 166.9 (s, NC_5H_4(ipso-C), 146.2 (d, NC_5H_4, $^1J_{C-H}$ = 169 Hz), 135.5 (d, NC_5H_4, $^1J_{C-H}$ = 158 Hz), 120.8 (d, NC_5H_4, $^1J_{C-H}$ = 163 Hz), 106.7 (d, NC_5H_4, $^1J_{C-H}$ = 164 Hz), 77.1 (s, $C(CH_3)_3$), 52.3 (td, Y-CH_2, $^1J_{C-H}$ = 143 Hz, $^1J_{Y-C}$ = 6 Hz), 52.1 (s, $C(CH_3)_3$), 37.0 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 125 Hz), 32.0 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 128 Hz), 8.2 (q, Si(CH_3)$_2$, $^1J_{C-H}$ = 118 Hz). Anal Calcd. (found) for $C_{26}H_{54}N_3O_2Si_2Y$: C: 53.31 (53.35); H: 9.29 (9.24); Y: 15.18 (15.21).

Preparation of [$Me_2Si(NCMe_3)(OCMe_3)$]$_2$Y-η^2(C,N)-CH_2-2-NC_5H_3-6-CH_3 (5.3). To a n-pentane solution (20 mL) of 2,6-dimethylpyridine (0.39 mL, 3.3 mmol), n-BuLi (1.3 mL, 2.5 M in hexanes, 3.3 mmol) was added at -30°C. The resulting yellow suspension was allowed to warm to room temperature and then stirred for an additional 20 minutes. Subsequently, 4.2 (2.0 g, 3.3 mmol) was added at -80°C. After warming to room temperature, the dark-yellow solution formed was stirred for 2 hours. The volatiles were removed in vacuo and the residue stripped with n-pentane (3 x 10 mL). Subsequently, the crude product was extracted with n-pentane (25 mL). Concentration and cooling to -80°C afforded 5.3 (0.61 g, 1.0 mmol, 31%) as yellow crystals. IR (KBr/Nujol, cm^{-1}): 2728 (w), 1601 (m), 1537 (m), 1526 (m), 1435 (s), 1395 (m), 1354 (m), 1316 (m), 1250 (s), 1221 (m), 1204 (m), 1179 (s), 1161 (m), 1055 (s), 1024 (m), 995 (w), 938 (s), 928 (s), 912 (s), 851 (s), 820 (s), 803 (m), 768 (s), 733 (s), 706 (m), 668 (w), 613 (m), 583 (w), 563 (w), 523 (w), 490 (w), 442 (w), 422 (w). ^{1}H NMR (benzene-d_6, δ): 6.74 (dd, 1H, NC_5H_3(H4), $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 6.8 Hz), 6.44 (d, 1H, NC_5H_3(H3), $^3J_{H-H}$ = 8.6 Hz), 5.81 (d, 1H, NC_5H_3(H5), $^3J_{H-H}$ = 6.8 Hz), 2.75 (d, 2H, Y-CH_2, $^2J_{Y-H}$ = 1.3 Hz), 2.43 (s, 3H, CH_3), 1.50 (s, 18H, C(CH_3)$_3$), 1.28 (s, 18H, C(CH_3)$_3$), 0.45 (s, 3H, Si(CH_3)$_2$), 0.40 (s, 3H, Si(CH_3)$_2$), 0.36 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ), 168.2 (s, NC_5H_3(ipso-C)), 154.5 (s, NC_5H_3(ipso-C)), 136.4 (d, NC_5H_3, $^1J_{C-H}$ = 156 Hz), 118.1 (d, NC_5H_3, $^1J_{C-H}$ = 163 Hz), 106.6 (d, NC_5H_3, $^1J_{C-H}$ = 163 Hz), 76.9 (s, $C(CH_3)_3$), 52.3 (s, $C(CH_3)_3$), 50.6 (td, Y-CH_2, $^1J_{C-H}$ = 142 Hz, $^1J_{Y-C}$ = 8 Hz), 37.2 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 123 Hz), 36.7 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 128 Hz), 32.0 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 124 Hz), 24.9 (q, CH_3, $^1J_{C-H}$ = 126 Hz), 8.0 (q, Si(CH_3)$_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd. (found) for $C_{27}H_{56}N_3O_2Si_2Y$: C, 54.06 (54.28); H, 9.41 (9.48); N, 7.01 (6.73); Y, 14.82 (14.72).

Preparation of [$Me_2Si(NCMe_3)(OCMe_3)$]$_2$Y-η^2(C,N)-$CH(CH_3)$-2-NC_5H_4 (5.4). To a THF solution (40 mL) of 2-ethyl-pyridine (0.38 mL, 3.5 mmol), n-BuLi (1.4 mL, 2.5 M in hexanes, 3.5 mmol) was added at -80°C to give an orange suspension. The reaction mixture was allowed to warm to room temperature and stirred for 1 hour. After the THF was evaporated, the remaining sticky solid was stripped with n-pentane (3 x 5 mL) and subsequently dissolved in toluene (40 mL). The orange-red solution was cooled to -80°C and 4.2 (2.0 g, 3.5 mmol) was added. After warming to room

temperature, the dark-orange solution formed was stirred for 20 hours. After the volatiles were removed *in vacuo*, the oily residue was stripped with *n*-pentane (3 x 15 mL) leaving an oily residue which did not solidify (1.3 g, 2.1 mmol, 60 %). The extreme solubility of **5.4** precluded further purification. ^{1}H NMR (benzene-d_6, δ): 7.64 (dd, 1H, NC$_5$H$_4$(H6), $^3J_{H-H}$ = 5.6 Hz, $^4J_{H-H}$ = 1.3 Hz), 6.78 (ddd, 1H, NC$_5$H$_4$(H4), $^3J_{H-H}$ = 7.7 Hz, $^3J_{H-H}$ = 5.6 Hz, $^4J_{H-H}$ = 0.9 Hz), 6.36 (d, 1H, NC$_5$H$_4$(H3), $^3J_{H-H}$ = 9.0 Hz), 5.74 (t, 1H, NC$_5$H$_4$(H5), $^3J_{H-H}$ = 6.0 Hz), 3.00 (qd, 1H, Y-CH(H)CH$_3$, $^3J_{H-H}$ = 5.6 Hz, $^2J_{Y-H}$ = 2.1 Hz), 1.78 (d, 3H, YCH(H)CH$_3$, $^3J_{H-H}$ = 5.6 Hz), 1.52 (s, 9H, C(CH$_3$)$_3$), 1.42 (s, 9H, C(CH$_3$)$_3$), 1.32 (s, 9H, C(CH$_3$)$_3$), 1.22 (s, 9H, C(CH$_3$)$_3$), 0.43 (s, 6H, Si(CH$_3$)$_2$), 0.39 (s, 3H, Si(CH$_3$)$_2$), 0.34 (s, 3H, Si(CH$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ): 162.2 (s, NC$_5$H$_4$(ipso-C)), 146.2 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 175 Hz), 135.5 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 155 Hz), 114.3 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 163 Hz), 103.4 (d, NC$_5$H$_4$, $^1J_{C-H}$ = 165 Hz), 77.4 (s, C(CH$_3$)$_3$), 60.9 (td, Y-C(H)CH$_3$, $^1J_{C-H}$ = 162 Hz, $^1J_{Y-C}$ = 5 Hz), 52.1 (s, C(CH$_3$)$_3$), 37.7 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 37.2 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 36.9 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 124 Hz), 33.0 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 31.8 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 12.8 (q, Y-C(H)CH$_3$, $^1J_{C-H}$ = 124 Hz), 8.2 (q, Si(CH$_3$)$_2$, $^1J_{C-H}$ = 118 Hz), 7.9 (q, Si(CH$_3$)$_2$, $^1J_{C-H}$ = 118 Hz).

Hydrogenation of [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(C,N)-NC$_5$H$_4$) (**5.1**). An NMR tube containing a solution of **5.1** (17 mg, 0.030 mmol) in benzene-d_6 (0.5 mL) was charged with hydrogen (4.6 atm). For 21 hours, the reaction was followed by ^{1}H NMR spectroscopy at 65 °C. The 45 ^{1}H NMR spectra, recorded at timed intervals, showed the gradual conversion of **5.1** into the 1,2-inserted product, [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y-NC$_5$H$_6$ (**5.5**, 96 % after 85 min.). While the intensity of resonances attributable to the 1,4-inserted product [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y-NC$_5$H$_6$ (**5.6**, 10 % after 20 h) and hydrogenated product, [Me$_2$Si(NCMe$_3$)(OCMe$_3$)]$_2$Y-NC$_5$H$_8$ (**5.7**, 46 % after 20 h) increased, the resonances of **5.1** and **5.5** subsided. Some Me$_2$Si(N(H)CMe$_3$)(OCMe$_3$) (14 % after 21 h) was also formed during the reaction. Separation and purification of the various reaction products proved to be impossible due to their high solubility. **5.5**: ^{1}H NMR (benzene-d_6, δ): 7.01 (d, 1H, NC$_5$H$_6$(H6), $^3J_{H-H}$ = 6.4 Hz), 6.24 (ddd, 1H, NC$_5$H$_6$(H4), $^3J_{H-H}$ = 5.6 Hz, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 0.9 Hz), 5.20 (td, 1H, NC$_5$H$_6$(H5), $^3J_{H-H}$ = 6.4 Hz, $^4J_{H-H}$ = 0.9 Hz), 4.87 (m, 1H, NC$_5$H$_6$(H3)), 4.29 (m, 2H, NC$_5$H$_6$(H2, H2')), 1.39 (s, 18H, C(CH$_3$)$_3$), 1.36 (s, 18H, C(CH$_3$)$_3$), 0.37 (s, 12H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d_6, δ), 144.3 (s, NC$_5$H$_6$), 127.5 (s, NC$_5$H$_6$), 101.9 (s, NC$_5$H$_6$), 94.8 (s, NC$_5$H$_6$), 78.8 (s, C(CH$_3$)$_3$), 52.0 (s, C(CH$_3$)$_3$), 47.5 (s, NC$_5$H$_6$(C2)), 37.1 (s, C(CH$_3$)$_3$), 31.6 (s, C(CH$_3$)$_3$), 7.8 (s, Si(CH$_3$)$_2$). **5.6**: ^{1}H NMR (benzene-d_6, δ): 6.45 (dd, 2H, NC$_5$H$_6$(H2, H6), $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.3 Hz), 4.48 (dt, 2H, NC$_5$H$_6$(H3, H5), $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 3.0 Hz), 3.54 (td, 2H, NC$_5$H$_6$(H4, H4'), $^3J_{H-H}$ = 3.0 Hz, $^4J_{H-H}$ = 1.7 Hz), 1.47 (s, 18H, C(CH$_3$)$_3$), 1.34 (s, 18H, C(CH$_3$)$_3$), 0.35 (s, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ), 135.8 (d, NC$_5$H$_6$(C2, C6), $^1J_{C-H}$ = 162 Hz), 94.7 (d, NC$_5$H$_6$(C3, C5), $^1J_{C-H}$ = 158 Hz), 79.1 (s, C(CH$_3$)$_3$), 52.0 (s, C(CH$_3$)$_3$), 37.1 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 129 Hz), 31.5 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 126 Hz), 23.7 (t, NC$_5$H$_6$(C4), $^1J_{C-H}$ = 126 Hz), 7.7 (q, Si(CH$_3$)$_2$, $^1J_{C-H}$ = 118 Hz). **5.7**: ^{1}H NMR (benzene-d_6, δ): 6.87 (d, 1H, NC$_5$H$_8$(H6), $^3J_{H-H}$ = 7.3 Hz), 4.51 (m, 1H, NC$_5$H$_8$(H5)), 3.61 (m, 2H, NC$_5$H$_8$(H4, H4')), 2.42 (m, 2H, NC$_5$H$_8$(H2, H2')), 1.94 (m, 2H, NC$_5$H$_8$(H3, H3'), 1.40 (s, 18H, C(CH$_3$)$_3$), 1.37 (s, 18H, C(CH$_3$)$_3$), 0.38 (s, 12H, Si(CH$_3$)$_2$). ^{13}C NMR (benzene-d_6, δ), 139.2 (d, NC$_5$H$_8$(C6), $^1J_{C-H}$ = 153 Hz), 87.8 (d, NC$_5$H$_8$(C5), $^1J_{C-H}$ = 159 Hz), 78.5 (s, C(CH$_3$)$_3$), 51.9 (s, C(CH$_3$)$_3$), 47.0 (t, NC$_5$H$_8$(C2), $^1J_{C-H}$ = 133 Hz), 37.1 (q, C(CH$_3$)$_3$, $^1J_{C-H}$ = 128

Hz), 31.5 (q, $C(CH_3)_3$, $^1J_{C-H}$ 126 Hz), 25.0 (t, $NC_5H_6(C3)$, $^1J_{C-H}$ = 126 Hz), 23.8 (t, $NC_5H_8(C4)$, $^1J_{C-H}$ = 126 Hz), 7.8 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 118 Hz).

Determination of Rate Constants of the Hydrogenation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2-(C,N)-NC_5H_4)$ (5.1). The rate constants were calculated from the collected experimental data with non-linear regression techniques, using theoretically derived expressions (appendix). The decline of 5.1 follows pseudo-first-order kinetics, since a ln([5.1])-versus-time plot gives a straight line. Therefore, the data points were fitted to the exponential function $[5.1]_t = [5.1]_0 \cdot e^{-k'At}$. The non-linear regression resulted in a curve with $r^2 = 0.998$ and $k'_A = 8.3(\pm 0.2)\cdot10^{-4}$ s^{-1}. Dividing k'_A by the dihydrogen concentration ($[H_2]_0$ = 0.075 mol·L^{-1}) yielded $k_A = 1.1(\pm 0.1)\cdot10^{-2}$ L·mol^{-1}·s^{-1}. The $[H_2]_0$ was calculated using the solubility constant α = 0.1 $cm^3 \cdot g^{-1} \cdot atm^{-1}$.[32] k_B was calculated using the rate expression for the isomerization of 5.5 into 5.6 (appendix) and the data points collected from t = 0 to 10 hours. Inserting k'_A in the theoretical expression resulted in a curve with r^2 = 0.996 and $k_B = 1.3(\pm 0.2)\cdot10^{-5}$ s^{-1}. For the final step, the rate constant was derived from the increase in 5.7 after 1.4 hours (d[5.1]/dt = 0). Inserting k'_A and k_B in the rate equation resulted in a curve with r^2 = 0.999 and $k'_C = 4.0(\pm 0.2)\cdot10^{-5}$ s^{-1}. Dividing k'_C by the dihydrogen concentration yielded $k_C = 5.3(\pm 0.3)\cdot10^{-4}$ L·mol^{-1}·s^{-1}.

NMR Tube Reaction of 5.1 with Ethylene. An NMR tube containing a solution of 5.1 (56 mg, 0.10 mmol) in benzene-d_6 (0.5 mL) was charged with ethylene (4.7 atm., 0.27 mmol) and heated to 50°C. The ^{1}H NMR spectra collected during the reaction showed the slow formation of 5.4. The reaction is not clean and considerable amounts of thermolysis products were formed. After 65 h at 50°C, 95 % of 5.1 had been consumed to give a mixture (^{1}H NMR) of 5.4 (36 %), $Me_2Si(N(H)CMe_3)(OCMe_3)$ (15 %), 2-ethylpyridine (15 %) and isobutene (19 %).

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$-C•CPh.Py (5.8). HC≡CPh (7.8 µL, 0.071 mmol) was added to an NMR tube charged with a solution of 5.1 (40 mg, 0.070 mmol) in benzene-d_6 (0.5 mL). After one hour at room temperature, nearly all 5.1 had reacted, yielding a mixture of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$-C≡CPh.Py (5.8, 51 %) and $Me_2Si(N(H)CMe_3)(OCMe_3)$ (37 %). Addition of 16 µL (0.15 mmol) of HC≡CPh resulted in fast protolysis of the alkoxysilylamido ligands (^{1}H NMR). 5.8: ^{1}H NMR (benzene-d_6, δ): 9.62 (s (broad), 2H, NC_5H_5(H2+H6)), 7.68 (dd, 2H, o-C_6H_5, $^3J_{H-H}$ = 8.1 Hz, $^4J_{H-H}$ = 1.3 Hz), 7.13 (t, 2H, m-C_6H_5, $^3J_{H-H}$ = 7.7 Hz), 6.99 (t, 1H, p-C_6H_5, $^3J_{H-H}$ = 7.3 Hz), 6.85 (t (broad), 1H, NC_5H_5(H4), $^3J_{H-H}$ = 6.8 Hz), 6.59 (t (broad), 2H, NC_5H_5(H3+H5), $^3J_{H-H}$ = 6.4 Hz), 1.53 (s, 18H, $C(CH_3)_3$), 1.48 (s, 18H, $C(CH_3)_3$), 0.59 (s, 6H, $Si(CH_3)_2$), 0.45 (s, 6H, $Si(CH_3)_2$).

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y$-C•CPh.THF.(pentane)$_{0.5}$ (5.9). To a toluene solution (20 mL) of 4.2 (1.50 g, 2.5 mmol), NaC≡CPh (0.31 g, 2.5 mmol) was added at -80°C. The initially white suspension turned light orange within 10 minutes. After stirring for 30 minutes at room temperature, the solvent was removed in vacuo and the resulting brown oil was stripped with n-

pentane (3 x 7 mL). Extraction with n-pentane (10 mL), concentration of the extracts and cooling to -30°C gave 5.9 (0.77 g, 1.1 mmol, 44 %) as a white microcrystalline powder. Repeated recrystalization from n-pentane yielded colorless bar shaped crystals of 5.9, suitable for an X-ray structure analysis. Since the crystals rapidly lost solvent (n-pentane) from the crystal lattice, satisfactory elemental analyses could not be obtained. IR (KBr/Njol, cm^{-1}): 3075(w), 3056(w), 2955(s), 2926(s), 2855(s), 2723(w), 2674(w), 1640(m), 1595(m), 1481(m), 1465(s), 1377(s), 1370(s), 1356(m), 1304(w), 1250(s), 1208(s), 1196(s), 1179(s), 1114(w), 1067(s), 1056(s), 1034(m), 1024(m), 992(w), 942(sh), 930(s), 914(s), 881(w), 851(s), 820(s), 802(w), 791(w), 772(s), 751(s), 735(s), 700(m), 692(m), 669(w), 615(w), 521(m), 490(w), 428(w). ^{1}H NMR (benzene-d_6, δ): 7.59 (d, 2H, o-C_6H_5, $^3J_{H-H}$ = 8.3 Hz), 7.09 (t, 2H, m-C_6H_5, $^3J_{H-H}$ = 7.7 Hz), 6.96 (t, 1H, p-C_6H_5, $^3J_{H-H}$ = 6.8 Hz), 4.05 (m, 4H, THF α-CH_2), 1.61 (s, 18H, C(CH_3)$_3$), 1.47 (s, 18H, C(CH_3)$_3$), 1.38 (m, 4H, THF β-CH_2), 1.23 (m, 3H, n-pentane-CH_2), 0.88 (t, 3H, n-pentane-CH_3, $^3J_{H-H}$ = 6.7 Hz), 0.49 (s, 6H, Si(CH_3)$_2$), 0.39 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 145.3 (d, Y-C≡C-Ph, $^1J_{Y-C}$ = 53 Hz), 131.3 (d, C_6H_5, $^1J_{C-H}$ = 159 Hz), 128.1 (d, C_6H_5, $^1J_{C-H}$ = 159 Hz), 125.5 (d, C_6H_5, $^1J_{C-H}$ = 161 Hz), 108.1 (dt, Y-C≡C-Ph, $^2J_{Y-C}$ = 5 Hz, $^3J_{C-H}$ = 11 Hz), 77.6 (s, $C(CH_3)_3$), 70.5 (t, THF α-CH_2, $^1J_{C-H}$ = 149 Hz), 52.0 (s, $C(CH_3)_3$), 37.1 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 123 Hz), 31.8 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 125 Hz), 25.1 (t, THF β-CH_2, $^1J_{C-H}$ = 133 Hz), 22.9 (t, n-pentane-CH_2, $^1J_{C-H}$ = 126 Hz), 14.2 (q, n-pentane-CH_3, $^1J_{C-H}$ = 124 Hz), 8.1 (q, Si(CH_3)$_2$, $^1J_{C-H}$ = 118 Hz), 7.8 (q, Si(CH_3)$_2$, $^1J_{C-H}$ = 117 Hz).

Preparation of [Me_2Si(NCMe$_3$)(OCMe$_3$)]$_2$Y-C•CPh (5.10). Compound 5.9 (0.50 g, 0.7 mmol) was stripped with toluene (3 x 5 mL) and subsequently dried *in vacuo* until all the THF resonances in the ^{1}H NMR spectrum of the product had disappeared. Then, the product was dissolved in n-pentane (7 mL). Crystallization at -80°C yielded 5.10 (0.39 g, 0.64 mmol, 91 %) as white needles. IR (KBr/Nujol, cm^{-1}): 3074 (w), 3056 (w), 2723 (w), 2674 (w), 2174 (w), 1593 (m), 1481 (m), 1407 (m), 1397 (m), 1370 (m), 1356 (m), 1250 (s), 1221 (m), 1208 (m), 1198 (m), 1177 (m), 1069 (m), 1055 (m), 1036(m), 1024 (m), 930 (s), 914 (s), 851 (s), 818 (s), 802 (m), 774 (s), 754 (m), 737 (s), 691 (m), 671 (w), 615 (m), 519 (m), 505 (m), 490 (m), 471 (w), 420 (w). ^{1}H NMR (benzene-d_6, δ): 7.57 (d, 2H, o-C_6H_5, $^3J_{H-H}$ = 8.2 Hz), 7.09 (t, 2H, m-C_6H_5, $^3J_{H-H}$ = 7.3 Hz), 6.98 (t, 1H, p-C_6H_5, $^3J_{H-H}$ = 7.3 Hz), 1.62 (s, 18H, $C(CH_3)_3$), 1.40 (s, 18H, C(CH_3)$_3$), 0.42 (s, 6H, Si(CH_3)$_2$), 0.38 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (benzene-d_6, δ): 144.2 (d, Y-C≡C-Ph, $^1J_{Y-C}$ = 60 Hz), 131.5 (d, C_6H_5, $^1J_{C-H}$ = 160 Hz), 128.3 (d, C_6H_5, $^1J_{C-H}$ = 159 Hz), 126.0 (d, C_6H_5, $^1J_{C-H}$ = 157 Hz), 108.9 (dt, Y-C≡C-Ph, $^2J_{Y-C}$ = 5 Hz, $^2J_{C-H}$ = 12 Hz), 79.1 (s, $C(CH_3)_3$), 52.2 (s, $C(CH_3)_3$), 37.1 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 121 Hz), 31.5 (q, C(CH_3)$_3$, $^1J_{C-H}$ = 126 Hz), 8.0 (q, Si(CH_3)$_2$, $^1J_{C-H}$ = 118 Hz), 7.6 (q, Si(CH_3)$_2$, $^1J_{C-H}$ = 117 Hz). Anal. Calcd. (found) for $C_{28}H_{53}N_2O_2Si_2Y$: C, 56.54 (56.67); H, 8.98 (8.96); Y, 14.95 (15.03).

Preparation of [Me_2Si(NCMe$_3$)(OCMe$_3$)]$_2$Y(η^2-(N,N')-N=C(Ph)-2-NC_5H_4) (5.11). N≡CPh (11.0 μL, 0.108 mmol) was added to an NMR tube containing a benzene-d_6 (0.4 mL) solution of 5.1 (59 mg, 0.103 mmol). Upon addition, the red solution turned intensely purple. The ^{1}H NMR spectrum recorded

after 10 min. at room temperature showed that all 5.1 had reacted, to give 5.11. ^{1}H NMR (benzene-d_6, δ): 9.04 (d, 1H, NC_5H_4(H6), $^3J_{H-H}$ = 4.6 Hz), 7.74 (d, 2H, o-C_6H_5, $^3J_{H-H}$ = 6.8 Hz), 7.25 (t, 2H, m-C_6H_5, $^3J_{H-H}$ = 7.3 Hz), 7.17 (m, 2H, NC_5H_4(H3) + p-C_6H_5), 7.05 (td, 1H, NC_5H_4(H4), $^3J_{H-H}$ = 7.6 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.61 (ddd, 1H, NC_5H_4(C5), $^3J_{H-H}$ = 6.4 Hz, $^3J_{H-H}$ = 5.1 Hz, $^4J_{H-H}$ = 1.2 Hz), 1.41 (s broad, 36H, $C(CH_3)_3$), 0.44 (s, 6H, $Si(CH_3)_2$), 0.39 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6): 161.3 (s, NC_5H_4(ipso-C)), 156.7 (s, N=C), 151.1 (d, Ar, $^1J_{C-H}$ = 179 Hz), 144.0 (s, C_6H_5(ipso-C)), 140.0 (d, Ar, $^1J_{C-H}$ = 164 Hz), 128.1 (d, Ar, $^1J_{C-H}$ = 158 Hz), 128.0 (d, Ar, $^1J_{C-H}$ = 158 Hz), 127.4 (d, Ar, $^1J_{C-H}$ = 159 Hz), 122.2 (d, Ar, $^1J_{C-H}$ = 166 Hz), 121.9 (d, Ar, $^1J_{C-H}$ = 166 Hz), 76.4 (s, $C(CH_3)_3$), 51.8 (s, $C(CH_3)_3$), 37.4 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 121 Hz), 37.1 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 122 Hz), 31.8 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 127 Hz), 8.1 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 117 Hz), 7.7 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 118 Hz).

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N(H)-C(Ph)=C(H)-2-$NC_5H_4)$ (5.12b). To an NMR tube charged with a solution of 5.2 (39 mg, 0.067 mmol) in benzene-d_6 (0.5 mL), N≡CPh (6.9 μL, 0.068 mmol) was added. Upon addition of the benzonitrile, the solution changed from yellow to orange-red. The ^{1}H NMR spectrum recorded directly after the NMR tube was filled, showed resonances characteristic for $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N=C(Ph)-$CH_2$-2-$NC_5H_4)$ (5.12a) and $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N(H)-C(Ph)=C(H)-2-$NC_5H_4)$ (5.12b). After 2h at room temperature, all 5.12a was converted into 5.12b. 5.12a: ^{1}H NMR (benzene-d_6, δ): 9.41 (dd, 1H, NC_5H_4(H6), $^3J_{H-H}$ = 6.4 Hz, $^4J_{H-H}$ = 2.1 Hz), 8.00 (d, 2H, o-C_6H_5, $^3J_{H-H}$ = 6.8 Hz), 7.35 (t, 2H, m-C_6H_5, $^3J_{H-H}$ = 6.8 Hz), 7.20 (t, 1H, p-C_6H_5, $^3J_{H-H}$ = 6.8 Hz), 6.93 (td, 1H, NC_5H_4(H4), $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.63 (m, 2H, NC_5H_4(H3 + H5)), 4.59 (d, 1H, CH_2, $^2J_{H-H}$ = 14.3 Hz), 4.18 (d, 1H, CH_2, $^2J_{H-H}$ = 14.3 Hz), 1.54 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 0.50 (s, 6H, $Si(CH_3)_2$), 0.41 (s, 6H, $Si(CH_3)_2$). 5.12b: ^{1}H NMR (benzene-d_6, δ): 9.18 (s (broad), 1H, NC_5H_4(H6)), 7.75 (d, 2H, o-C_6H_5, $^3J_{H-H}$ = 7.3 Hz), 7.17 (m, 3H, m+p-C_6H_5), 6.87 (t, 1H, NC_5H_4(H4), $^3J_{H-H}$ = 7.3 Hz), 6.80 (s (broad), 1H, N-H), 6.72 (d, 1H, NC_5H_4(H3), $^3J_{H-H}$ = 8.1 Hz), 6.27 (t, 1H, NC_5H_4(C5), $^3J_{H-H}$ = 6.4 Hz), 5.47 (s broad, 1H, =C-H), 1.62 (s, 9H, $C(CH_3)_3$), 1.50 (s, 9H, $C(CH_3)_3$), 1.31 (s, 9H, $C(CH_3)_3$), 1.20 (s, 9H, $C(CH_3)_3$), 0.50 (s, 3H, $Si(CH_3)_2$), 0.47 (s, 3H, $Si(CH_3)_2$), 0.41 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6): 163.6 (s, NC_5H_4(ipso-C)), 159.9 (s, C(Ph)=CH), 147.2 (d, Ar, $^1J_{C-H}$ = 170 Hz), 135.7 (d, Ar, $^1J_{C-H}$ = 163 Hz), 128.7 (d, Ar, $^1J_{C-H}$ = 162 Hz), 128.2 (d, Ar, $^1J_{C-H}$ = 160 Hz), 126.1 (d, Ar, $^1J_{C-H}$ = 157 Hz), 124.3 (d, Ar, $^1J_{C-H}$ = 162 Hz), 111.4 (d, Ar, $^1J_{C-H}$ = 165 Hz), 93.4 (d, C(Ph)=CH, $^1J_{C-H}$ = 151 Hz), 76.8 (s, $C(CH_3)_3$), 52.1 (s, $C(CH_3)_3$), 37.2 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 123 Hz), 32.0 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 125 Hz), 8.0 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 117 Hz).

NMR Tube Reaction of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(C,N)-2-$NC_5H_4)$ (5.1) with N≡CMe. Acetonitrile (5.0 μL, 0.096 mmol) was added to a solution of 52 mg (0.091 mmol) of 5.1 in benzene-d_6 (0.5 mL). An instantaneous color change from red-brown to brown-yellow occurred. The ^{1}H NMR spectrum taken after 10 minutes at room temperature, showed resonances of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-N,N')-N=C(Me)-2-$NC_5H_4)$ (5.13a). Within hours at room temperature, 5.13a rearranged into $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-N,N')-N(H)-C(=$CH_2$)-2-$NC_5H_4)$ (5.13b). 5.13a: ^{1}H NMR (benzene-d_6, δ): 9.00 (d, 1H, NC_5H_4(H6), $^3J_{H-H}$ = 4.7 Hz), 7.10 (dd, 1H, NC_5H_4(H3), $^3J_{H-H}$ = 7.3 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.96 (td, 1H, NC_5H_4(H4), $^3J_{H-H}$ = 7.7 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.58 (ddd, 1H,

NC_5H_4(H5), $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-H}$ = 4.7 Hz, $^4J_{H-H}$ = 1.3 Hz), 2.45 (s, 3H, CH_3), 1.47 (s, 18H, $C(CH_3)_3$), 1.32 (s, 18H, $C(CH_3)_3$), 0.49 (s, 12H, $Si(CH_3)_2$).

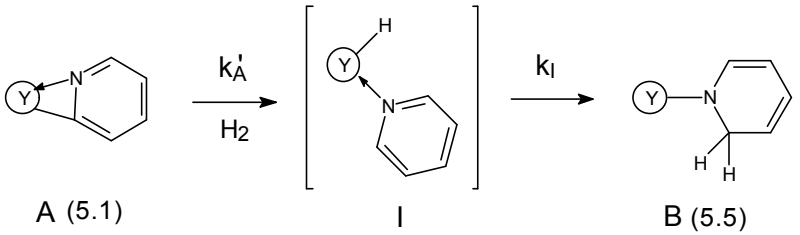
Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N(H)-C(=$CH_2$)-2-$NC_5H_4$) (5.13b) Acetonitrile (120 µL, 2.3 mmol) was added to a solution of 5.1 (1.3 g, 2.2 mmol) in hexanes (15 mL). After 24 hours at room temperature, the volatiles were removed *in vacuo*, leaving a brown sticky solid. After stripping (3 x 5 mL) with hexanes, the solid was redissolved in hexanes (5 mL) and cooled to -80°C for crystallization. Repeated recrystallization from hexanes yielded 5.13b (0.9 g, 1.4 mmol, 65 %) as red-brown crystalline material. IR (KBr, Nujol, cm^{-1}): 2955 (s), 2924(vs), 2855(s), 1572(m), 1561(sh), 1464(s), 1393(sh), 1370(m), 1354(w), 1248(s), 1219(sh), 1208(s), 1181(s), 1134(w), 1071(s), 1032(w), 930(s), 910(w), 851(s), 810(s), 766(m), 731(s), 664(w), 649(w), 613(w), 561(w), 521(w), 488(w), 444(w). ^{1}H NMR (benzene-d_6, δ): 9.17 (d, 1H, NC_5H_4(H6), $^3J_{H-H}$ = 4.3 Hz), 7.66 (d, 1H, NC_5H_4(H3), $^3J_{H-H}$ = 8.1 Hz), 6.99 (t, 1H, NC_5H_4(H4), $^3J_{H-H}$ = 7.3 Hz), 6.65 (t, 1H, NC_5H_4(H5), $^3J_{H-H}$ = 6.0 Hz), 4.99 (s (broad), 1H, NH), 4.50 (s, 1H, =CH(H)H), 4.20 (s, 1H, =CH(H)H), 1.56 (s, 9H, $C(CH_3)_3$), 1.54 (s, 9H, $C(CH_3)_3$), 1.17 (s, 9H, $C(CH_3)_3$), 1.11 (s, 9H, $C(CH_3)_3$), 0.48 (s, 12H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6): 162.3 (s, NC_5H_4(ipso-C)), 156.9 (s, $C(=CH_2)$), 149.8 (d, NC_5H_4, $^1J_{C-H}$ = 181 Hz), 137.1 (d, NC_5H_4, $^1J_{C-H}$ = 162 Hz), 121.3 (d, NC_5H_4, $^1J_{C-H}$ = 164 Hz), 121.1 (d, NC_5H_4, $^1J_{C-H}$ = 164 Hz), 78.5 (t, $=CH_2$, $^1J_{C-H}$ = 155 Hz), 77.1 (s, $C(CH_3)_3$), 76.6 (s, $C(CH_3)_3$), 51.9 (s, $C(CH_3)_3$), 37.1 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 124 Hz), 31.9 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 126 Hz), 29.3 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 125 Hz), 7.9 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd. (found) for $C_{27}H_{55}N_4O_2Si_2Y$: C, 52.92 (52.14); H, 9.05 (8.75); N, 9.14 (9.05); Y, 14.51 (14.35).

Preparation of $[Me_2Si(NCMe_3)(OCMe_3)]_2Y(\eta^2$-(N,N')-N(H)-C(Me)=C(H)-2-NC_6H_4) (5.14b). To a toluene solution (20 mL) of 5.2 (0.52 g, 0.89 mmol), acetonitrile (48 µL, 0.92 mmol) was added at -80°C. The solution was allowed to warm to room temperature and stirred for 4 hours after which the solvent was evaporated. Extraction of the yellow residue with pentane (10 mL) followed by concentration and cooling to -80°C, afforded 5.14b (0.43 g, 0.69 mmol, 77%) as yellow crystals. IR (KBr/Nujol, cm^{-1}) 1613 (w), 1580 (s), 1512 (s), 1404 (s), 1370 (m), 1352 (m), 1339 (s), 1246 (m), 1208 (m), 1179 (m), 1155 (m), 1061 (m), 1024 (w), 990 (w), 936 (s), 910 (m), 849 (s), 818 (m), 764 (m), 743 (m), 729 (s), 664 (w), 637 (w), 611(w), 521 (w), 490 (w). ^{1}H NMR (benzene-d_6, δ): 9.10 (s (broad), 1H, NC_6H_4(H6)), 6.84 (ddd, 1H, NC_6H_4(H4), $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 1.7 Hz), 6.61 (d, 1H, NC_6H_4(H3), $^3J_{H-H}$ = 8.6 Hz), 6.22 (s (broad), 1H, NH), 6.20 (td, 1H, NC_6H_4(H5), $^3J_{H-H}$ = 6.8 Hz, $^4J_{H-H}$ = 1.3 Hz), 5.02 (d (broad), 1H, =CH, $^4J_{H-H}$ = 2.1 Hz), 1.93 (s, 3H, CH_3), 1.55 (s, 18H, $C(CH_3)_3$), 1.23 (s, 18H, $C(CH_3)_3$), 0.50 (s, 6H, $Si(CH_3)_2$), 0.44 (s, 3H, $Si(CH_3)_2$), 0.41 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6, δ): 162.0 (s, NC_5H_4(ipso-C)), 159.5 (s, C(Ph)=CH), 147.3 (d (broad), NC_5H_4, $^1J_{C-H}$ = 173 Hz), 135.5 (d, NC_5H_4, $^1J_{C-H}$ = 160 Hz), 123.2 (d, NC_5H_4, $^1J_{C-H}$ = 162 Hz), 110.5 (d, NC_5H_4, $^1J_{C-H}$ = 166 Hz), 92.7 (d, C(Ph)=CH, $^1J_{C-H}$ = 154 Hz), 76.6 (s, $C(CH_3)_3$), 52.0 (s, $C(CH_3)_3$), 37.1 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 125 Hz), 31.9 (q, $C(CH_3)_3$, $^1J_{C-H}$ = 126 Hz), 29.3 (q, CH_3, $^1J_{C-H}$ = 124 Hz), 7.9 (q, $Si(CH_3)_2$, $^1J_{C-H}$ = 118 Hz). Anal. Calcd. (found) for $C_{28}H_{57}N_4O_2Si_2Y$: C, 53.65 (53.44); H, 9.17 (8.97); N, 8.94 (9.00); Y, 14.18 (14.08).

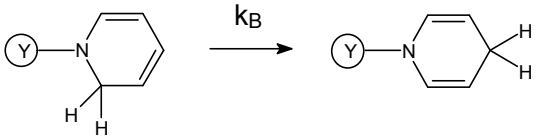
Preparation of $\{[Me_2Si(NCMe_3)(OCMe_3)]_2Y\}_2\{\mu,\eta^2,\eta^2\text{-}(N,N',O)\text{-}OC\text{-}(2\text{-}NC_5H_4)_2\}$ (5.15). A Schlenk flask (200 mL) containing a red-brown solution of 5.1 (5.0 g, 0.87 mmol) inn-pentane (20 mL) was degassed and charged with CO (1 atm.). The color of the solution instantaneously turned purple. After 20 hours at room temperature, the color of the solution had changed to deep blue. Evaporation of the volatiles gave 5.15 (0.72 g, 0.61 mmol, 70 %) as a microcrystalline powder. IR (KBr/Nujol, cm^{-1}) 3079 (w), 2726 (w), 1597 (m), 1544 (w), 1532 (m), 1518 (w), 1404 (s), 1383 (s), 1370 (s), 1356 (s), 1273 (w), 1246 (m), 1221 (m), 1208 (m), 1179 (s), 1146 (s), 1090 (m), 1069 (m), 1062(m), 1032 (m), 1025 (m), 988 (m), 970 (m), 932 (s), 910 (m), 897 (m), 851 (s), 818 (m), 802 (m), 766 (m), 746 (m), 733 (s), 665 (w), 633 (m), 615 (m), 575 (w), 523 (m), 490 (m), 469 (w), 428 (w). ^{1}H NMR (benzene-d_6, δ): 9.04 (s (broad), 1H, NC_5H_4(H6)), 7.65 (d, NC_5H_4(H3), $^3J_{H\text{-}H}$ = 8.8 Hz), 7.04 (t, 1H, NC_5H_4(H4), $^3J_{H\text{-}H}$ = 6.5 Hz), 5.93 (m, 1H, NC_5H_4(H5)), 1.52 (s, 9H, $C(CH_3)_3$), 1.48 (s, 9H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 1.30 (s, 9H, $C(CH_3)_3$), 0.54 (s, 3H, $Si(CH_3)_2$), 0.52 (s, 3H, $Si(CH_3)_2$), 0.47 (s, 3H, $Si(CH_3)_2$), 0.45 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (benzene-d_6, δ): 149.2 (s, ipso-C), 147.3 (s, ipso-C), 146.9 (d, NC_5H_4, $^1J_{C\text{-}H}$ = 166 Hz), 133.5 (d, NC_5H_4, $^1J_{C\text{-}H}$ = 158 Hz), 120.1 (d, NC_5H_4, $^1J_{C\text{-}H}$ = 159 Hz), 104.7 (d, NC_5H_4, $^1J_{C\text{-}H}$ = 164 Hz), 78.0 (s, $C(CH_3)_3$), 77.1 (s, $C(CH_3)_3$), 52.5 (s, $C(CH_3)_3$), 51.9 (s, $C(CH_3)_3$), 37.4 (q, $C(CH_3)_3$, $^1J_{C\text{-}H}$ = 124 Hz), 37.0 (q, $C(CH_3)_3$, $^1J_{C\text{-}H}$ = 124 Hz), 32.4 (q, $C(CH_3)_3$, $^1J_{C\text{-}H}$ = 126 Hz), 31.7 (q, $C(CH_3)_3$, $^1J_{C\text{-}H}$ = 126 Hz), 8.2 (q, $Si(CH_3)_2$, $^1J_{C\text{-}H}$ = 118 Hz), 7.9 (q, $Si(CH_3)_2$, $^1J_{C\text{-}H}$ = 118 Hz). Anal. Calcd. (found) for $C_{54}H_{104}N_6O_5Si_4Y_2$: C, 52.28 (52.04); H, 8.95 (9.01); N, 7.17 (7.07); Y, 15.18 (15.08).

Appendix.

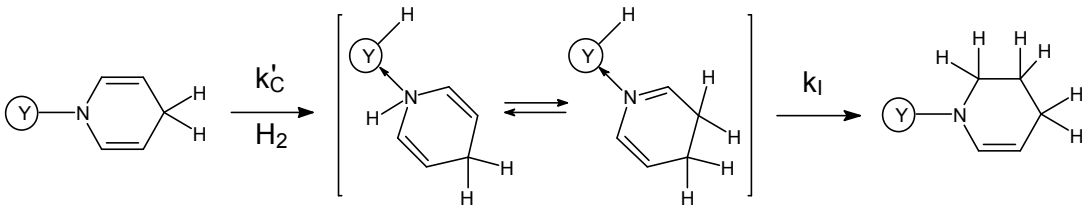
Equations:



A (5.1) I B (5.5) (1)



B (5.5) C (5.6) (2)



C (5.6) I' D (5.7) (3)

Assumptions:

$$\frac{d[H_2]}{dt} = 0 \qquad \frac{d[I]}{dt} = 0 \qquad \frac{d[I']}{dt} = 0$$

Rate expressions:

$$\frac{d[A]}{dt} = -k'_A\cdot[A] \qquad \frac{d[B]}{dt} = k'_A\cdot[A] - k_B\cdot[B] \qquad \frac{d[C]}{dt} = k_B\cdot[B] - k'_C\cdot[C] \qquad \frac{d[D]}{dt} = k'_C\cdot[C]$$

$$k'_A = k_A\cdot[H_2] \qquad k'_C = k_C\cdot[H_2]$$

$$[A]_t = [A]_0\cdot e^{-k'_A\cdot t}$$

$$[B]_t = \frac{k'_A\cdot[A]_0}{k_B - k'_A}\left(e^{-k'_A\cdot t} - e^{-k_B\cdot t}\right)$$

$t > 1.4$ h, $e^{-k'_A\cdot t} \longrightarrow 0$

$$[C]_t = \frac{k'_A\cdot k_B\cdot[A]_0}{\left(k'_C - k'_A\right)\left(k'_C - k_B\right)} e^{-k'_C\cdot t} - \frac{k'_A\cdot k_B\cdot[A]_0}{\left(k_B - k'_A\right)\left(k'_C - k_B\right)} e^{-k_B\cdot t}$$

$$[D]_t = \frac{k'_A\cdot k_B\cdot[A]_0}{\left(k'_C - k'_A\right)\left(k'_C - k_B\right)}\left(1 - e^{-k'_C\cdot t}\right) + \frac{k'_A\cdot k'_C\cdot[A]_0}{\left(k_B - k'_A\right)\left(k'_C - k_B\right)}\left(1 - e^{-k_B\cdot t}\right) + \frac{k_B\cdot k'_C\cdot[A]_0}{\left(k_B - k'_A\right)\left(k'_C - k'_A\right)}$$

References and Notes.

1 (a) Watson, P. L. J. Chem. Soc., Chem. Commun. 1983, 276-277. (b) Tompson, M. E.; Bercaw, J. E. Pure Appl. Chem. 1984, 56, 1-11. (c) Den Haan, K. H.; Wielstra, Y.; Teuben, J. H.; Organometallics 1987, 6, 2053-2060. (d) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. J. Am. Chem. Soc. 1987, 109, 203-219. (e) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. Organometallics 1993, 12, 3531-3540.

2 (a) Deelman, B.-J.; Stevels, W. M.; Lakin, M. T.; Spek, A. L.; Teuben, J. H. Organometallics 1994, 13, 3881-3891. (b) Deelman, B.-J. Ph. D. Thesis, University of Groningen, 1994.

3 (a) Klei, E.; Teuben, J. H. J. Organomet. Chem. 1981, 214, 53-64. (b) Klei, E. Ph. D. Thesis, University of Groningen, 1981.

4 For example see: Jordan, R.F.; Guram, A. S. Organometallics 1990, 9, 2116-2123 and references cited therein.

5 (a) Schumann, H.; Lauke, H.; Hahn, E.; Pickardt, J. J. Organomet. Chem. 1984, 263, 29-35. (b) Schumann, H.; Albrecht, I.; Pickardt, J.; Hahn, E. J. Organomet. Chem. 1984, 276, C5-C9. (c) Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. Organometallics 1985, 4, 1836-1841. (d) Den Haan, K. H. Ph. D. Thesis, University of Groningen, 1986.

6 For example see: (a) Jordan, R. F.; Taylor, D. F. J. Am. Chem. Soc. 1989, 111, 778-779. (b) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. Organometallics 1990, 9, 1546-1557. (c) Guram, A. S.; Jordan, R. F. Organometallics 1991, 10, 3470-3479.

7 (a) Guram, A. S.; Jordan, R. F.; Taylor, D. F. J. Am. Chem. Soc. 1991, 113, 1833-1835. (b) Guram, A. S.; Swenson, D. C.; Jordan, R. F. J. Am. Chem. Soc. 1992, 114, 8991-8996.

8 Lithiation of pyridine, α-picoline, lutidine and 2-ethyl-pyridine were carried out in either pentane, ether or THF at -80°C, using n-BuLi. See also: Colgan, D.; Papasergio, R. I.; Raston, C. L.; White, A. H. J. Chem. Soc., Chem. Commun. 1984, 1708-1710.

9 Crystal data for $C_{26}H_{54}N_3O_2Si_2Y$: M = 585.81, monoclinic, spacegroup $P2_1/n$, a = 16.757(1) Å, b = 12.170(1) Å, c = 17.454(1) Å, β = 112.401°, V = 3290.8(4) Å^3 and D_{calc} = 1.182 g.cm^{-3} for Z = 4. The structure was solved by Patterson methods and refined to R_F = 0.060 and wR = 0.056 for 4741 unique reflections with $I \geq 2.5\ \sigma(I)$ and 497 parameters.

10 Recknagel, A.; Steiner, A.; Brooker, S.; Stalke, D.; Edelmann, F. T. J. Organomet. Chem. 1991, 415, 315-326.

11 Den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. Organometallics 1986, 5, 1726-1733.

12 (a) Rogers, R. D.; Atwood, J. L.; Ernad, A.; Sikora, P. J.; Rausch, M. D. J. Organomet. Chem. 1981, 216, 383-392. (b) Den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. Organometallics 1987, 6, 1509-1515. (c) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. Inorg. Chem. 1986, 25, 3614-3619.

13 For example see: (a) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M. Reingold, A. L.; Stern, C. L.; Marks, T. J. J. Am. Chem. Soc. 1994, 116, 10212-10240. (b) Booij, M.; Kiers, N.

H.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L.Organometallics 1989, 8, 2454-2461. (c) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Olofson, J. M.J. Organomet. Chem. 1989, 376, 311-320. (d) See also Chapter 3, 4 and 6.

14 (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. Organometallics 1983, 2, 1252-1254. (b) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L.J. Am. Chem. Soc. 1984, 106, 1291-1300. (c) Reger, D. L.; Lindeman, J. A.; Lebioda, L.Inorg. Chem. 1988, 27, 3923-3929.

15 (a) Bailey, S. I.; Colgan, D.; Engelhardt, L. M.; Leung, W.-P; Papasergio, R. I.; Raston, C. L.; White, A. H.J. Chem. Soc., Dalton Trans.1986, 603-613. (b) Guram, A.; S.; Swenson, D. C.; Jordan, R. F.J. Am. Chem. Soc.1992, 114, 8991-8996. (c) Beshouri, S. M.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P.Organometallics 1990, 9, 2375-2385. (d) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P.Inorg. Chem.1981, 20, 1496-1500.

16 (a) March, J. Advanced Organic Chemistry, Reactions, Mechansims and Structure, 3rd ed.; John Wiley and Sons: New York,1985. (b) Joule, J. A.; Smith, G. F.Heterocyclic Chemistry; Van Nostrand Reinhold Company: London,1972.

17 The reaction of 5.2 and 5.3 with hydrogen is similar to that observed for 5.1, although the reaction rate decreases dramatically with increasing steric bulk. Hence, thermolysis of the complexes becomes substantial. Duchateau, R.; Brussee, E. A. C. Teuben, J. H. unpublished results.

18 Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T.Organometallics1986, 5, 443-450.

19 Nolan, S. P.; Stern, D.; Marks, T. J.J. Am. Chem. Soc.1989, 111, 7844-7853.

20 (a) Gagné, M. R.; Stern, C. L.; Marks, T. J.J. Am. Chem. Soc. 1992, 114, 275-294. (b) Giardell, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J.J. Am. Chem. Soc. 1994, 116, 10241-20154. (c) Li, Y.; Fu, P.-F.; Marks, T. J.Organometallics 1994, 13, 439-440.

21 Berno, P.; Gambarotta, S.J. Chem. Soc., Chem. Commun.1994, 2419-2421.

22 See appendix for used assumptions and the forthcoming rate-equations.

23 (a) Schaverien, C. J.;Organometallics1994, 13, 69-82. (b) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H.J. Am. Chem. Soc.1993, 115, 4931-4932. (c) Stern, D.; Sabat, M.; Marks, T. J.J. Am. Chem. Soc.1990, 112, 9558-9575.

24 (a) Evans, W. J.; Keyer, R. A.; Ziller, J. W.Organometallics 1990, 9, 2628-2631. (b) Heeres, H. J.; Nijhof, J.; Teuben, J. H.Organometallics 1993, 12, 2609-2617. (c) Evans, W. J.; Keyer, R. A.; Ziller, J. W.Organometallics1994, 12, 2618-2633. (d) Forsyth, C. M.; Nolan, S. P.; Stern, C. L.; Marks, T. J.Organometallics1993, 12, 3618-3623.

25 Crystal data for $C_{32}H_{61}N_2O_3Si_2Y.(C_5H_{12})_{0.5}$: M = 703.00, monoclinic,C2/c, a = 21.041(1) Å,b = 19.321(1) Å,c = 21.437(1) Å,β = 107.946(6)°, V = 8290.9(8) Å^3 and D_{calc} = 1.126 g.cm^{-3} for Z = 8. The structure was solved by Patterson methods and refined to R_F = 0.045 and wR = 0.041 for 5735 unique observed reflections with ≥ 2.5 σ(I) and 628 parameters.

26 Den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H.J. Organomet. Chem.1987, 323, 181-192.

27 Evans, W. J.; Ulibarry, T. A.; Chamberlain, L. R.; Ziller, J. W.; Alvarez, D., Jr. Organometallics 1990, 9, 2124-2130.

28 (a) Atwood, J. L.; Hains, C. F.; Jr.; Tsutsui, M.; Gebala, A. E. J. Chem. Soc., Chem. Commun. 1973, 452-453. (b) Atwood, J. L.; Tsutsui, M.; Ely, N.; Gebala, A. E. J. Coord. Chem. 1976, 5, 209-215. (c) Evans, W. J.; Bloom, I.; Doedens, R. J. J. Organomet. Chem. 1984, 265, 249-255.

29 (a) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. J. Am. Chem. Soc. 1982, 104, 2008-2015. (b) Heeres, H. J. Ph. D. Thesis, University of Groningen, 1990.

30 (a) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. J. Chem. Soc., Chem. Commun. 1992, 124-126. (b) Evans, W. J.; Wayda, A. D.; Hunter, W. E.; Atwood, J. L. J. Chem. Soc., Chem. Commun. 1981, 706-708. (c) Jeske, G.; Schock, L. E.; Swepton, P. N.; Schumann, H.; Marks, T. J. J. Am. Chem. Soc. 1985, 107, 8091-8103.

31 Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. J. Chem. Soc., Chem. Commun. 1976, 522-523.

32 Bartels, J.; Borchers, H.; Hausen, H.; Hellwege, K. H.; Schäfer, K. L.; Schmidt, E. Landolt-Börnstein, Zahlenwerte und Functionen, 6th ed., Vol. 2, Springer-Verlag: Berlin, 1962.